

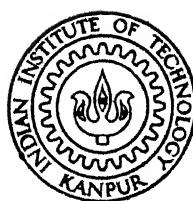
VIBRATIONAL DYNAMICS AND PHASE  
TRANSITIONS IN TETRAMETHYL  
AMMONIUM COMPOUNDS

By

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# VIBRATIONAL DYNAMICS AND PHASE TRANSITIONS IN TETRAMETHYL AMMONIUM COMPOUNDS

A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
**DOCTOR OF PHILOSOPHY**

*By*  
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*to the*

**DEPARTMENT OF PHYSICS**

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CERTIFICATE

This is to certify that the work presented in this thesis entitled "VIBRATIONAL DYNAMICS AND PHASE TRANSITIONS IN TETRAMETHYL AMMONIUM COMPOUNDS" is carried out by Mr. Mahendra Pal under my supervision and has not been submitted elsewhere for a degree or diploma.

Date: March 9, 1984.

  
H D Bist  
Professor of Physics

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## SYNOPSIS

### VIBRATIONAL DYNAMICS AND PHASE TRANSITIONS IN TETRAMETHYL AMMONIUM COMPOUNDS

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Tetramethyl ammonium halides (abbreviated as TMACl, TMABr and TMAI for chloride, bromide and iodide, respectively) and tetramethyl ammonium tetrachloro zincate (abbreviated as  $(\text{TMA})_2\text{ZnCl}_4$ ) have been taken up for detailed temperature dependent Raman studies in view of the following facts :

- (i) The present vibrational assignments of the modes for the TMA moiety are controversial in solution as well as in the solid phases;
- (ii) The TMA halides, in general, are isostructural at room temperature with space group  $D_{4h}^7$  ( $z = 2$ ), but only TMACl is known to undergo four successive phase transitions between 4 and 540 K;
- (iii) The nature and mechanism of these phase transitions in TMACl are not yet clearly understood;
- (iv)  $(\text{TMA})_2\text{ZnCl}_4$  undergoes several successive phase transitions including an incommensurate phase between 296.65 and 280.95 K.

On the basis of these studies we have been able to provide

detailed vibrational assignments for the observed bands in all the salts. Further we have been able to observe all the reported phase transitions in TMACl above liquid nitrogen temperature and specify their characteristics at each of the transition temperatures. We have also confirmed the incommensurate phase in  $(\text{TMA})_2\text{ZnCl}_4$  through Raman spectra.

Chapter 1 of the thesis reviews the various aspects of vibrational spectroscopy, such as vibrations in molecules and crystals, group theoretical analysis, mechanical and electrical anharmonicities, Fermi resonance, isotope effect etc. The different types of phase transitions and various experimental techniques used for their investigations are also reviewed in this chapter.

Chapter 2 contains details of the techniques used with 'Spex Ramalog spectrophotometer system' for Raman spectra and 'Perkin Elmer 580' for infrared spectra, and accessories such as the low and high temperature cells fabricated in our laboratory for Raman studies, and 'Specac variable temperature cell' used for infrared studies. The technique for obtaining temperatures below the normal boiling point of liquid nitrogen (upto 63 K, the freezing point), viz. evaporating the coolant at lower pressure, has also been described here.

In Chapter 3, the vibrational assignments of the observed Raman and infrared bands in aqueous solutions and in various phases of normal ( $d_0$ ) and perdeuterated ( $d_{12}$ ) tetramethyl ammonium chloride are proposed on the basis of polarization

data and concentration dependence of intensity in aqueous solutions, and the splitting of the bands on lowering the temperature in the polycrystalline samples. For explaining the occurrence of three intense and polarized bands in the  $\text{CH}_3$  stretching region, which switch over intensities on variation of concentration, a model is proposed according to which the  $T_d$  symmetry of TMA ion dynamically distorts to  $C_{3v}$ . The three phase transitions in  $\text{TMACl-d}_0$  above liquid nitrogen temperatures have been confirmed on the basis of these studies. Numbering the phases from high temperature downwards, the following inferences have been drawn from the spectra :

(i) The phase transition  $\text{II} \rightleftharpoons \text{I}$ , occurring at 536 K, is due to ionic diffusion in which H atoms of TMA get relatively free.

(ii) The transition  $\text{III} \rightarrow \text{II}$  is irreversible and of the reconstructive type and this transition temperature depends on the rate of heating. The transition occurs at  $367 \pm 2$  K on keeping the sample under continuous vacuum during investigation.

(iii) The transition  $\text{III} \rightleftharpoons \text{IV}$  occurs at 185 K and is due to reorientation of  $\text{CH}_3$  groups and tumbling of the whole TMA moiety. In  $\text{TMACl-d}_{12}$  a phase transition ( $\text{III} \rightarrow \text{II}$ ) at  $407 \pm 5$  K is only observed and it is also irreversible and of the reconstructive type. It is concluded that  $\text{TMACl-d}_{12}$  lies in between  $\text{TMACl-d}_0$  and  $\text{TMABr-d}_0$  in the generalized phase diagram of the TMA halides.

Chapter 4 deals with the temperature dependent Raman studies of TMABr and TMAI. The splitting of  $C_4N$  totally symmetric mode  $\nu_3(A_1)$  in the iodide is discussed in terms of a disordered structure. The temperature induced variations of intensities of the components suggests occupation of two different sites which correspond to the different orientations of TMA : parallel and perpendicular. Their energy difference is deduced to be  $0.43 \text{ KCal. mol}^{-1}$ . The relative behaviours of the three halides are explained if the tumbling motion is governed by the free space available in the lattice in the three salts. It is in the order  $I^- > Cl^- > Br^-$ . A comparative study of selectively deuterated tetramethyl ammonium iodides ( $TMAI-d_n$ ;  $n = 0, 1, 3, 9, 10, 11, 12$ ) samples is also presented in this chapter.

In Chapter 5, the Raman studies of single crystals of  $(TMA)_2ZnCl_4$  in six polarization geometries are presented. The behaviour of the internal modes of TMA and  $ZnCl_4^{--}$  in the incommensurate phase is particularly discussed.

Chapter 6 outlines the conclusions drawn from our studies and also gives some suggestions and prospects for future work.

## 1. INTRODUCTION

With the invention of lasers, the Raman scattering technique has become as powerful a tool as infrared absorption for the analysis and identification of materials and for the study of molecular dynamics and molecular structure [1]. Extensive information about the structure and symmetry of molecules as well as their vibrational energies can be obtained from these spectra. This chapter is intended as an introduction to the principles and practice of those aspects of Raman and infrared spectroscopy which are of major interest in our present research work.

### 1.1 THE DYNAMICS OF A MOLECULE

The dynamics of an isolated  $N$ -atomic molecule can be obtained in terms of  $3N$  degrees of freedom. These may be classified as 3 translations + 3 rotations +  $(3N-6)$  vibrations for a non-linear molecule or 3 translations + 2 rotations +  $(3N-5)$  vibrations for a linear molecule. The vibrations of a molecule are described in terms of normal modes. A normal mode has the following properties [2,3] : (i) each atom of the system oscillates about its equilibrium position with simple harmonic motion having the same frequency and phase, and (ii) the relative velocities and amplitudes of individual atoms depend on their masses, and the nature of motion is so governed that no resultant translation or rotation of the

system as a whole takes place.

The vibrations of an isolated molecule in the gas phase are subject only to the symmetry restrictions based on its own intrinsic point group symmetry. The methods of classification of normal modes of a free molecule using group theoretical approach have been discussed by several workers [3-5].

Vibrational assignments of the observed frequencies of different modes of vibration are made by studying the infrared and Raman spectra of a molecule in vapour, liquid and solid phases and the state of polarization of Raman lines. Due to mathematical complexity only in a very few cases of simple molecules it has been possible to determine these vibrational frequencies on a purely theoretical basis. Analytical expressions for force constants as explicit functions of the observed frequencies and geometric parameters cannot generally be obtained. The only way for calculating the force constants from the observed frequencies is to use an iterative method. A starting set of force constants is assumed and refined by successive approximations until the set which yields the calculated frequencies in best agreement with the observed one is obtained. These studies lead to a knowledge of the structure of the molecules, like bond lengths, bond angles etc. The results are not always unique and isotopic substitution is often required to verify the force constants.

When a group of atoms constituting an ion or a molecule goes to build up a crystal, its normal modes usually undergo

three types of modifications : (i) splitting of degenerate vibrations, (ii) multiplicity due to the unit cell containing more than one molecule, and (iii) alternations in the selection rules. The vibrational potential energy ( $V$ ) associated with a unit cell under harmonic approximation can be expressed as [6,7]

$$V = \sum_j (V_j^0 + V_j') + \sum_j \sum_k V_{jk} + V_L + \sum_j V_{Lj} \quad (1.1)$$

where the summations extend over all the molecular units in the unit cell. The various terms are :

- $V_j^0$  - the potential energy function of the free  $j^{\text{th}}$  molecule. It determines the internal mode vibrations.
- $V_j'$  - the perturbation of  $V_j^0$  due to the equilibrium field of the crystal at the site of the  $j^{\text{th}}$  molecule. It can cause shifts in the fundamental frequencies and changes in selection rules.
- $V_{jk}$  - represents terms involving displacement coordinates in the  $j^{\text{th}}$  and  $k^{\text{th}}$  molecules i.e. it encompasses interactions between vibrations in different molecules.
- $V_L$  - contains terms involving the relative displacement and rotational orientation of molecules with respect to each other, and thus represents the lattice potential.
- $V_{Lj}$  - denotes those terms involving interaction between lattice coordinates and the internal coordinates of the  $j^{\text{th}}$  molecule.

A molecule in a crystalline array can, in principle, be treated as an entity by itself, subject only to symmetry restrictions arising out of the crystalline environment. But the interaction between this entity and rest of the crystal which creates the environment cannot be ignored. For complete rigour, therefore, the entire array of molecule must be analysed as one unit. However, such a completely rigorous approach is essentially impossible for practical reasons. Therefore, the vibrational spectra of crystals are always analysed with some approximations.

#### 1.1.1 Unit Cell Approach

The first systematic approach to explain the solid state spectra was made by Bhagavantam and Venkatarayudu [8, 9]. They treated the unit cell as one giant molecule and applied the group theoretical method to examine its vibrations. In this approach the problem of classification of  $3nN$  modes of the whole crystal (containing  $n$  unit cells of  $N$  atoms each) is reduced to the problem of classification of  $3N$  modes of the unit cell. Such a simplification is based on the assumption that atoms or molecules at equivalent lattice positions in different unit cells are in the same state of motion without any phase differences.

#### 1.1.2 Local or Site Symmetry Approach

There is another powerful method to distribute the normal modes of ions or molecules in solid state phase.

Assuming the local potentials to be mainly responsible for the dynamics of polyatomic groups in the crystals, Halford [10] suggested the classification of the normal modes into species of local symmetry point group. It is achieved by correlating the symmetry species of the point group of the free molecular group to those of local symmetry point group. A serious limitation of this method is that it neglects the interaction between different groups in the same unit cell. Hornig [11] considered such interactions and showed that by further correlating the species of the site and the crystal symmetry point groups, one obtains the same classification as that obtained by the unit cell approach.

As an illustration consider the case of tetramethyl ammonium halides (TMAX,  $X = Cl, Br$  or  $I$ ) which belong to the tetragonal system with space group  $D_{4h}^7$  ( $Z = 2$ ) at room temperature [12-14]. The TMA ion has the point group symmetry  $T_d$ . In the unit cell the TMA and  $X^-$  ions have site symmetries  $D_{2d}$  and  $C_{4v}$ , respectively; whereas the unit cell is invariant only under the operations of the factor group  $D_{4h}$ . Since  $D_{2d}$  and  $C_{4v}$  are the local or site symmetries for TMA and  $X^-$  ions, respectively, a correlation between the species of  $T_d$ ,  $D_{2d}$  and  $D_{4h}$  gives the distribution of the modes of TMA ions, while the modes of  $X^-$  ions are distributed by correlating the species of  $C_{4v}$  and  $D_{4h}$ .

Winston and Halford [15] derived both the methods by considering the motions of a crystal segment composed of an

arbitrary number of unit cells and subjecting it to the Born-Von Karman boundary conditions [16]. The applications of these methods (unit cell approach and site symmetry approach) have been discussed in depth [17-23]. However, we will discuss in detail the distributions of the modes of tetramethyl ammonium halides and tetramethyl ammonium tetrachlorozincate in Chapters 3 and 5, respectively.

## 1.2 ANHARMONICITY AND INTERACTION OF VIBRATIONS

Anharmonicity affects molecular vibrations in two important ways [3,24]. Firstly, the selection rule derived for the harmonic oscillator  $\Delta v = \pm 1$  ( $v$  - vibrational quantum number) ceases to be a rigorous selection rule and transitions with  $\Delta v = \pm 1, \pm 2, \pm 3 \dots$  become allowed. Secondly, the vibrational energy levels are not spaced apart equally by the quantity  $h\nu$ . And finally, combination bands are also allowed. The intensity of the overtone or combination bands is directly related to the anharmonicity character of the vibrations. If overtones or combination bands are not observed, the harmonic approximation is an excellent one. Observation of strong overtone or combination bands indicate the presence of anharmonic character in the vibration.

The anharmonicities are of two types : mechanical and electrical [25,26]. The mechanical anharmonicity is associated with the deviation of the potential function for a given mode from the harmonic form. Normal vibrations rest

on the assumption that in the range of amplitude of oscillations involved the quadratic term in the potential energy plays the dominant role in the motions. But in actual vibrations the cubic, quartic and higher terms in the potential energy may be appreciable to make the oscillations anharmonic. The potential energy function for a particular vibration is written as

$$V = \frac{1}{2} K_2 Q^2 + K_3 Q^3 + K_4 Q^4 + \dots \quad (1.2)$$

where  $Q$  is the relevant normal coordinate and  $K_i$  the force constant.

Electrical anharmonicity depends on the quadratic and higher terms in the expression of the instantaneous dipole moment given by

$$u = u_0 + u_1 Q + u_2 Q^2 + \dots \quad (1.3)$$

There are cases where the mechanical vibration is harmonic ( $K_3, K_4, \dots = \text{zero}$ ), but the changes in  $u$  are anharmonic ( $u_2, u_3, \dots = \text{finite}$ ).

The mechanical anharmonicity is related to vibrations through the well known equation [3]

$$G(v) = (v + \frac{1}{2}) w_e - (v + \frac{1}{2})^2 w_e x_e + \dots \quad (1.4)$$

where  $G(1)-G(0)$ ,  $G(2)-G(0)$ , ... give the observed band frequencies  $v$ ,  $2v$  etc. Conversely, the observed values of  $v$  and  $2v$  [not the same as  $2(v)$ ] lead to  $w_e$ ,  $w_e x_e$  [3] and cubic potential constant  $K_3$  [25]. Also the relative

intensities of  $\nu$  and  $2\nu$  bands lead to  $\mu_2/\mu_1$  [26]. The relations are :

$$w_e X_e = \frac{2(\nu) - 2\nu}{2} \quad (1.5)$$

$$w_e = \nu + 2w_e X_e \quad (1.6)$$

$$K_3 = \pm \left[ \frac{4}{15} w_e |w_e X_e| \right]^{1/2} \quad (1.7)$$

$$\frac{\mu_2}{\mu_1} = \frac{- (K_3/w_e) \pm \left[ I_{2\nu} \cdot \nu / I_\nu \cdot 2\nu \right]^{1/2}}{1 \pm 5(K_3/w_e) \left[ I_{2\nu} \cdot \nu / I_\nu \cdot 2\nu \right]^{1/2}} \quad (1.8)$$

where + sign in the last two equations refers to a negative value of  $w_e X_e$  and vice versa.

### 1.3 FERMI RESONANCE

Fermi observed that two or more quasi-degenerate vibrational levels of the same symmetry repel each other. The interaction is due to the presence of anharmonic terms in the vibrational potential function and consequent mixing of the related vibrational wave functions [3, 27]. The phenomenon is called Fermi resonance.

#### 1.3.1 Two Levels Fermi Resonance

Consider two quasi-degenerate energy levels having unperturbed wave functions  $\psi_1^0$  and  $\psi_2^0$  with unperturbed energies  $E_1^0$  and  $E_2^0$ , respectively. The first order perturbation wave function will be

$$\begin{aligned}\Psi_1 &= a\Psi_1^0 + b\Psi_2^0 \\ \Psi_2 &= -b\Psi_1^0 + a\Psi_2^0\end{aligned}\quad (1.9)$$

$$\text{where } a^2 + b^2 = 1.$$

According to the first order perturbation theory, the perturbed energies ( $\lambda$ ) and eigenfunctions can be obtained by solving the secular equation

$$\begin{vmatrix} E_1^0 - \lambda & |H'_{12}| \\ H'_{21} & E_2^0 - \lambda \end{vmatrix} = 0 \quad (1.10)$$

where  $H'$  is the interaction hamiltonian. This gives

$$\lambda = \frac{1}{2} (E_1^0 + E_2^0) \pm \frac{1}{2} [4|H'_{12}|^2 + (E_1^0 - E_2^0)^2]^{1/2} \quad (1.11)$$

Thus the perturbed levels separation (which is the observed one) is

$$\delta = [4|H'_{12}|^2 + \delta_0^2]^{1/2} \quad (1.12)$$

where  $\delta_0 (= E_1^0 - E_2^0)$  is the separation of the unperturbed levels and  $|H'_{12}|$  is called Fermi coupling coefficient.

Bertran et al. [28] calculated the coefficients  $a$  and  $b$  of eq. (1.9) to be

$$a = \left[ \frac{\delta + \delta_0}{2} \right]^{1/2}, \quad b = \left[ \frac{\delta - \delta_0}{2} \right]^{1/2} \quad (1.13)$$

The matrix elements of the actual transitions are

$$\langle 0 | A | 1 \rangle = a \langle 0 | A | 1^0 \rangle + b \langle 0 | A | 2^0 \rangle$$

$$\langle 0 | A | 2 \rangle = -b \langle 0 | A | 1^0 \rangle + a \langle 0 | A | 2^0 \rangle \quad (1.14)$$

where  $A$  is polarizability ( $\alpha$ ) for Raman transitions and dipole moment ( $p$ ) for infrared transitions.

The ratio of intensities of the transitions is, thus,

$$R = \frac{I_1^0}{I_2^0} = \frac{|\langle 0 | A | 1 \rangle|^2}{|\langle 0 | A | 2 \rangle|^2} = \frac{a^2 I_1^0 + b^2 I_2^0}{-b^2 I_1^0 + a^2 I_2^0} \quad (1.15)$$

Here  $I_1^0$  and  $I_2^0$  are the unperturbed intensities of the resonating bands. Setting  $I_1^0/I_2^0 = R_0$  and using equations (1.15), (1.13) and (1.12) we obtain

$$R = \left[ \frac{\{\delta + (\delta^2 - 4|H_{12}^t|^2)^{1/2}\}^{1/2} R_0^{1/2} + \{\delta - (\delta^2 - 4|H_{12}^t|^2)^{1/2}\}^{1/2}}{-\{\delta - (\delta^2 - 4|H_{12}^t|^2)^{1/2} R_0^{1/2} + \{\delta + (\delta^2 - 4|H_{12}^t|^2)^{1/2}\}^{1/2}} \right]^{1/2} \quad (1.16)$$

The above equation contains two unknowns,  $R_0$  and  $H_{12}^t$  and, therefore, cannot be solved without further information. However, Fermi resonance occurs mostly in the cases where one of the transitions of the Fermi doublet is a strong fundamental and the other is a very weak harmonic or combination transition (i.e.  $I_2^0 \approx 0$ ). Then

$$R = \frac{I_1^0}{I_2^0} = \frac{\delta + \delta_0}{\delta - \delta_0} \quad (1.17)$$

Thus the observed  $\delta$  and  $R$  lead to  $\delta_0$ , and hence to  $|H_{12}^t|$  from eq. (1.12). For simpler molecules (e.g.  $\text{CO}_2$  and

NCO radical) Eggers and Crawford [29] and Dixon [30] have found that the values of Fermi coupling coefficients calculated independently from the known anharmonic constants show only a slight mismatch with those calculated from the approximate equation (1.12). However, for complex molecules this cannot be checked as anharmonic constants are not usually known.

### 1.3.2 Three Levels Fermi Resonance

Dellepiane et al. [31] have extended the theoretical examination of Fermi resonance to a special case of three levels : two fundamentals and one overtone in solid N-methyl acetamide. The unperturbed positions of the fundamentals and the overtone were known in this case at room temperature. For Fermi resonance in a three levels system the secular equation, in general, will be

$$\begin{vmatrix} E_1^O - \lambda & H_{12}' & H_{13}' \\ H_{21}' & E_2^O - \lambda & H_{23}' \\ H_{31}' & H_{32}' & E_3^O - \lambda \end{vmatrix} = 0 \quad (1.19)$$

This equation is not solvable even for the case of one fundamental and two overtones under the assumption that the intrinsic intensities of overtones are very small (i.e.  $I_2^O \approx 0$  and  $I_3^O \approx 0$ ), as it still involves six unknown coefficients, whereas the observed transitions provide only five data. For Fermi resonance among more than three levels

the situation would be even worse.

### 1.3.3 Methods of Identifying Fermi Resonance

Fermi resonance is not the only origin of an anomalous doublet. It may also arise from association, solvation, conformational isomerism, hot bands etc. [28]. The presence of Fermi resonance can be established by the following methods:

#### (i) The method of isotopic substitution

Appropriate isotopic substitution may alter one of the transitions to remove the accidental degeneracy. The absence of perturbation in the substituted compound confirms that the presence of anomalous doublet in the parent compound was due to Fermi resonance.

#### (ii) The method of solvent variation

It consists in studying the observed doublet in solutions of the compound in a wide series of solvents. One can write a set of  $n$  equations of the types

$$R_i = F(\delta_i, R_{oi}, |H_{12}'|_i) \quad (1.20)$$

for  $n$  different solvents. A plot of  $R$  vs.  $\delta$  contains all the information of the system of  $n$  equations. The positions of the related transitions may vary from solvent to solvent. Therefore, the magnitude of Fermi interaction would also vary accordingly. It can be recognized as a change in the ratio of intensities of the doublet from one solvent to the

other [28, 32, 33]. A smooth R vs.  $\delta$  curve, thus confirms the presence of Fermi resonance.

#### 1.4 ISOTOPE EFFECT

The vibrational investigation of isotopes of polyatomic molecule is helpful in force constant calculations, assignments of vibrational modes and structural determinations. To quite a good approximation the isotopic molecules have the same electronic structure and the potential function as the parent molecule.

##### 1.4.1 The Teller-Redlich Product Rule

In order to overcome the tedious calculations in determining the isotopic shifts in the frequencies of a particular species for large molecules Teller and Redlich [3] have given a simple product rule : For two isotopic molecules the product of the  $\nu^s/\nu$  values for all vibrations of a given symmetry type is independent of the potential constants and depends only on the masses of the atoms and the geometrical structure of the molecule . The formula for any molecule is

$$\frac{\nu_1^s}{\nu_1} \frac{\nu_2^s}{\nu_2} \cdots \frac{\nu_f^s}{\nu_f} = \left[ \left( \frac{m_1}{m_1^s} \right)^\alpha \left( \frac{m_2}{m_2^s} \right)^\beta \cdots \cdots \cdots \right] \left( \frac{M^s}{M} \right)^t \left( \frac{I_x^s}{I_x} \right)^{\delta x} \left( \frac{I_y^s}{I_y} \right)^{\delta y} \left( \frac{I_z^s}{I_z} \right)^{\delta z}]^{1/2} \quad (1.21)$$

Here the superscript s stands for isotopic substituted quantities,  $\nu_1, \nu_2, \dots, \nu_f$  are the frequencies of f genuine vibrations of the symmetry type considered,  $m_1, m_2, \dots$  masses of the representative atoms of the various sets of equivalent atoms,  $\alpha, \beta, \dots$  are the number of vibrations (inclusive of non-genuine vibrations) each set contributes to the symmetry type considered,  $M$  is the total mass of the molecule,  $t$  is the number of transitions of symmetry type considered,  $I_x, I_y, I_z$  are the moments of inertia about the  $x, y$  and  $z$  axes through the centre of mass,  $\delta_x, \delta_y, \delta_z$  are 1 or 0 depending on whether or not the rotation about the  $x, y, z$  axis is a non-genuine vibration of the symmetry type considered. Both on the left and right hand side (in  $\alpha, \beta, \dots, t, \delta_x, \delta_y, \delta_z$ ) a degenerate vibration is counted only once.

Let us consider the case of  $(\text{CH}_3)_4\text{N}^+$  ion under point group symmetry  $T_d$ . The distribution of vibrations of any  $T_d$  symmetric molecule under the point group  $T_d$  are given in Table 1.1 [3]. Here there are no nuclei in general position ( $m = 0$ ). Nitrogen atom is on all elements of symmetry ( $m_0 = 1$ ). One set of nuclei (H atoms) are on the planes  $\sigma_d$  but on no other element of symmetry ( $m_d = 1$ ), one set of nuclei (C-atoms) lie on the three-fold axes ( $m_3 = 1$ ), no atom lies on two-fold axes ( $m_2 = 0$ ). Then the general equation for  $(\text{CH}_3)_4\text{N}^+$  ion becomes as given below [34]

$$\prod_{i=1}^3 \frac{\nu_i^D}{\nu_i^H} = \sqrt{\frac{m_H^D}{m_i^D}}^2 = 0.500 \text{ (A}_1\text{-modes)}$$

$$\begin{aligned}
 \frac{\nu_4^D}{\nu_4^H} &= \sqrt{\frac{m_H}{m_D}} = 0.707 \quad (\text{A}_2\text{-modes}) \\
 \frac{8}{\prod_{i=5}^8} \left( \frac{\nu_i^D}{\nu_i^H} \right) &= \sqrt{\left( \frac{m_H}{m_D} \right)^3} = 0.354 \quad (\text{E-modes}) \\
 \frac{12}{\prod_{i=9}^{12}} \left( \frac{\nu_i^D}{\nu_i^H} \right) &= \sqrt{\left( \frac{m_H}{m_D} \right)^4 \left( \frac{I_z^D}{I_z^H} \right)^1} \quad (\text{F}_1\text{-modes}) \\
 \frac{19}{\prod_{i=12}^{19}} \left( \frac{\nu_i^D}{\nu_i^H} \right) &= \sqrt{\left( \frac{m_H}{m_D} \right)^5 \left( \frac{m_H^D}{m_H^H} \right)^1} = 0.221 \quad (\text{F}_2\text{-modes}) \quad (1.22)
 \end{aligned}$$

If the symmetry of an isotopic molecule is lower than that of the ordinary molecules, it is necessary for applying the product rule to know the symmetry species of point group of lower symmetry.

## 1.5 STRUCTURAL PHASE TRANSITIONS

Structural phase transitions occur when a material changes its crystallographic structure as a result of variation in temperature, pressure or any other parameter like an applied electric or magnetic field [35]. Both microscopic and macroscopic properties of the system change with such phase transitions. Their studies are of importance for various applications of the materials, like use of ferroelectrics as piezoelectric components and pyroelectric detectors, computer core storage in magnetized ferrite rings, liquid crystal displays, etc. [35-38]. Various experimental techniques such

as X-ray diffraction, neutron diffraction, Hall coefficient, specific heat measurement, heat capacity measurement, elastic constant measurement, susceptibility measurement, ultrasonic wave propagation, Raman and infrared spectroscopic studies, etc. [39] have been used to investigate such phase transitions. Raman scattering studies of structural phase transitions have been reviewed by Fleury [40], Scott [41], Steigmeier [42] and Nakamura [43]. These are important because at least one component of the soft mode of a continuous structural phase transition is always Raman active below the phase transition temperature [36]. A further advantage of Raman technique is that it can provide information about the specific molecular motions involved in triggering the phase transition [44].

#### 1.5.1 Classification of Phase Transitions

Different types of phase transitions cannot be rigorously classified. For instance, although phase transitions are classified as those of the first order or the second order, there are numerous cases exhibiting features of both [37]. Moreover, there are many different criteria too for classification of phase transitions. However, some broad classifications are given below.

##### (i) Reversible and irreversible phase transitions

A phase transition in which the system returns to its initial phase on withdrawal of the agency or parameter which caused the phase transition is known as a reversible

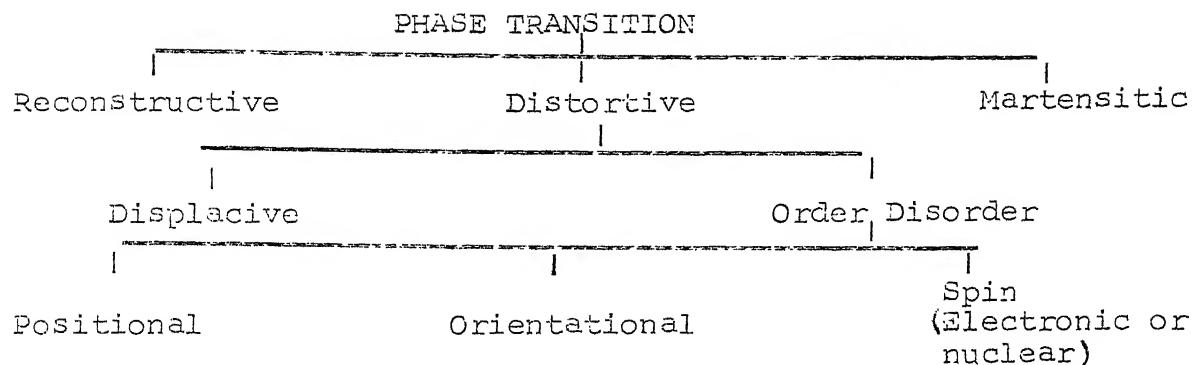
phase transition. But if the system does not do so, the transition is known as an irreversible phase transition. The change of graphite to diamond is an outstanding example of an irreversible phase transition.

(ii) The first order (or discontinuous) and second order (or continuous) phase transitions

A first order transition involves a sharp and discrete change in internal and free energies at the transition point. Therefore the system shows a discontinuity in almost all the physical and chemical properties at the transition point. In contrast the second order phase transitions occur over a wide range of the variable parameter. With temperature as the variable parameter these transitions are generally associated with increase of disorder and internal energy with rise in temperature, [45]. During a second order phase transition, the entropy and volume of the system remain continuous while the heat capacity and thermal expansivity undergo a discontinuous change [46]. The  $\lambda$ -transition is a particular case of second order transition in which the heat capacity tends towards infinity [37].

(iii) The Buerger classification

Buerger classifies the phase transitions according to the changes in crystal structure at the transition point [37, 47]. That is as follows :



In a reconstructive phase transition the original linkages of the net are disrupted and the atoms or molecules of the solid reconstruct a new lattice. Some typical transitions of the reconstructive type are : graphite to diamond [48], transformation of CsCl at  $479^{\circ}\text{C}$  [49] and of  $\text{NH}_4\text{Cl}$  at  $180^{\circ}\text{C}$  [37].

In a distortive phase transition the linkages of the net are not disrupted, but the regular lattice gets slightly distorted. This distortion may involve small displacements in the lattice positions of molecular units or may involve changes in the ordering of atoms or molecules among various equivalent positions (without altering the lattice type). Accordingly, the distortive phase transition is called a displacive or order-disorder type.

The various equivalent positions in the case of an order-disorder transition may refer to positions of atoms in the lattice or to angular orientations of molecules or ions or to spin of electrons or protons. Accordingly the order-disorder transition is called positional, orientational or

spin (electronic/nuclear) order-disorder type. Positional disorder has been observed in various inorganic compounds such as  $\text{AgI}$  [50],  $\text{RbAg}_4\text{I}_5$  [51] and  $\text{Fe}_3\text{O}_4$  [52]. Orientational disorder has been observed in  $\text{KCN}$  [53],  $\text{NaNO}_2$  [54] and  $\text{NH}_4\text{Cl}$  [55].

A distinction between the displacive and order-disorder type transitions is possible on the basis of atomic single cell potential [36]. This is schematically shown in Fig. 1.1 for one spatial coordinate  $Q$ . The anharmonic potential used is  $V(Q) = aQ^2 + bQ^4$ , with  $a < 0$  and  $b > 0$ . This is a double well potential in which the height of the hump between the two minima is given by  $\Delta E = \frac{a^2}{4b}$ . For the case  $\Delta E \gg KT_c$  the transition occurs due to ordering between  $Q_0 + \sqrt{\frac{-a}{2b}}$  and  $Q_0 - \sqrt{\frac{-a}{2b}}$ . On the other hand, if we have  $\Delta E \ll KT_c$  a continuous cooperative displacement of atoms along  $Q$  is found as a function of temperature around  $T_c$ .

#### (iv) Incommensurate-commensurate phase transitions

The recent discovery of incommensurably distorted structures has important implications for the study of structural phase transitions [56]. In a few years numerous examples have become known of compounds having in certain temperature interval a structure without any space group symmetry, whereas outside that interval the structure is crystalline. The non-crystalline structure is not amorphous but is well ordered and may be described as a periodic distortion not fitting with the crystal periodicity. The study

of the behaviour of incommensurate phase is now a subject of utmost interest theoretically as well as experimentally [56-63]. Pynn [56] has suggested a model to explain the incommensurate phase as shown in Fig. 1.2.

Consider a uniform chain of atoms, equally spaced by  $a$  (Fig. 1.2A), is modulated by sinusoidal displacement whose wavelength is  $4a$  (Fig. 1.2B). Then every fourth atom is displaced by the same amount. The distorted structure (Fig. 1.2C) can thus be described in terms of a unit cell which is four times larger and contains four times as many atoms as the original one. Most previous reports on structural transitions described systems in which the unit cell size either remained the same or was changed by a simple multiple at the transition. However, it is certainly not a priori necessary for a lattice modulation to have a periodicity which is rational multiple of a unit cell size. An example of a modulation which does not satisfy this simple criterion and which is thus incommensurable with the undistorted lattice is shown in Fig. 1.2D. The atomic arrangement in the incommensurable phase is depicted in Fig. 1.2E. This phase has the remarkable property that no two atoms are displaced by the same distance from their positions in the undistorted phase. It is thus impossible to find any lattice translation which maps the crystal into itself.

The incommensurable phase has been observed both in metallic and insulating materials. The physical effects which

drive the transitions are somewhat different in the two cases. For the insulators it is often found that competing, short-range interatomic forces of different ranges and similar magnitudes give rise to an incommensurable modulated phase. To have an idea how this may arise, consider the monoatomic chain in Fig. 1.2A and suppose that only elastic forces between first and second neighbour atoms contribute to the energy. The latter may then be written as

$$U = \sum_{n=1}^N \left[ A_1 \sum_{i= \pm 1} (u_n - u_{n+i})^2 + A_2 \sum_{i= \pm 2} (u_n - u_{n+i})^2 \right] \dots \quad (1.23)$$

where  $u_n$  is the longitudinal displacement of the  $n^{\text{th}}$  atom from its lattice site and  $A_1$  and  $A_2$  are the first and second neighbour harmonic force constants, respectively.

Expanding the displacement as a Fourier series

$$u_n = \sum_q u_q \cos(qna) \quad (1.24)$$

and substituting in equation (1.23) one finds that the energy is given by

$$\begin{aligned} U &= 4 \sum_q u_q^2 [A_1 (1 - \cos(qa)) + A_2 (1 - \cos(2qa))] \\ &= 4 \sum_q u_q^2 A_q \end{aligned} \quad (1.25)$$

A sinusoidal modulation structure will be stable if  $A_q$  in equation (1.25) has a minimum value for a non zero wave vector  $q_0$ . Necessary conditions for this to occur are that

$$\frac{\partial A_q}{\partial q} = 0 ; \quad \frac{\partial^2 A_q}{\partial q^2} > 0 \quad (1.26)$$

at the wave vector  $q_0$ . These conditions imply that a modulation of wave vector  $q_0$  given by

$$\cos(q_0 a) = -A_1/4A_2 \quad (1.27)$$

will be stable provided  $A_1 < 4|A_2|$  and  $A_2 \leq 0$ .

For conducting materials, interesting incommensurable transitions result from the interaction between conduction electrons and the atomic lattice. These interactions give rise to effective long-range interatomic forces.

#### 1.6 EARLIER STUDIES ON TETRAMETHYL AMMONIUM HALIDES

Tetramethyl ammonium halides (abbreviated as TMACl, TMABr and TMAI for chloride, bromide and iodide, respectively) have been extensively studied for their vibrational dynamics [34, 64-84] and phase transitions [85-91]. The vibrational assignments of the modes of TMA ion are, however, not the same. The intensity pattern of the bands in the methyl stretching region in Raman spectra of TMA halides in aqueous solutions is quite complex. Anhouse and Tobin [70], Berg [34] and Kabisch and Klose [77] have all attributed this complexity due to Fermi resonance interactions, although their conclusions as regarding assignments of the bands are not identical. To explain the abnormally high intensities of the combination/overtone bands in this region Kabisch and

Klose [77] have also invoked the effect of ion association occurring in concentrated solutions. Recently, Kabisch and Möbius studied the methyl deformation [79] and Stretching [80] regions of selectively deuterated TMA ion ( $\text{TMA-d}_n^*$ ;  $n = 0, 1, 3, 9, 10, 11$  and  $12$ ) in aqueous solutions. They explained the non-appearance of polarized  $\text{CH}_3$  symmetric bending mode  $\nu_2(\text{A}_1)$  in  $\text{TMA-d}_0$  to the overlapping of the wavefunctions of  $\text{C}_4\text{N}^+$  skeleton and methyl groups, and the usual complexity in the intensity pattern of the bands in methyl stretching region to Fermi resonance interactions.

Aimone and Cachet [81] have studied the far-infrared (FIR) spectra of TMA halides and proposed a model for interionic potential energy calculation. Ratcliffe and Waddington [82] have used inelastic neutron scattering to determine the positions of the modes of TMA ions which are forbidden in vibrational spectra (Raman and IR) such as  $\text{CH}_3$  torsion modes  $\nu_4(\text{A}_2)$  and  $\nu_{12}(\text{F}_1)$  etc. Some IR absorption data at high pressure [83] and  $^{15}\text{N}$  substituted halides [84] are also available.

As regarding phase transitions, Chang and Westrum [85] measured the heat capacities of these halides between 5 and 300 K, and found a first order phase transition at 75.8 K and a  $\lambda$ -transition at 184.9 K in the chloride. Stammller [87] found a third phase transition at 536 K in the chloride by

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\*  $n$  denotes the number of H atoms replaced by D-atoms in  $(\text{CH}_3)_4\text{N}^+$ .

differential thermal analysis. He suggested that the compounds are free from hydrogen bonding. Gibson and Raab [89] found one phase transition at  $\sim 415$  K by proton magnetic resonance. They have also shown that methyl group reorientation occurs without noticeable tunneling, followed by pseudoisotropic reorientation of the cations at slightly higher temperatures. Ionic diffusion occurs only in phase I, and phase II is piezoelectric [89]. Pistorius and Gibson [81] have suggested the space groups  $C_{3v}^5$  ( $Z = 1$ ) and  $O_h^5$  ( $Z = 4$ ) for TMACl in phases II and I, respectively.

However, the vibrational study of these compounds offers fertile field in view of the following :

- (i) the vibrational assignments still need more insight, especially for the methyl modes.
- (ii) the three halides are isostructural, but only  $\text{TMACl-d}_0$  is known to undergo four successive phase transitions between 4 and 540 K.
- (iii) the nature and mechanism of these phase transitions are not yet clear.

#### 1.7 EARLIER STUDIES ON TETRAMETHYL AMMONIUM TETRAHALO METALLATES

Tetramethyl ammonium tetrahalo metallates  $[(\text{TMA})_2\text{MX}_4]$ ,  $\text{TMA} = (\text{CH}_3)_4\text{N}$ ,  $\text{M} = \text{Zn, Mn, Ni, Cu, Co, Fe}$  and  $\text{X} = \text{Cl, Br}$  are of special interest from the following points of view [92]. First of all, the occurrence of one or more phase

transitions below room temperature, which are commonly related to organic group motion, is known. Secondly, the sequence of phase transitions near room temperature occurs together with the existence of an incommensurate phase. This transition sequence is similar to that found in inorganic compounds of the same family, although in this case the set of transitions is located in wider and generally different temperature ranges. Finally, the  $A_2BX_4$  compounds are also interesting for a ferroelectric phase which remains down to very low temperatures in inorganic crystals but only for a few degrees when  $(CH_3)_4N$  groups are present. The sequences of successive phase transitions in tetramethyl ammonium tetrahalo metallates have been characterized by methods such as differential thermal analysis [93-95], inelastic neutron scattering [96-99], x-ray diffraction [100-106], specific heat measurement [95,107,108], thermal expansion measurement [92], dielectric measurement [109-115], electron paramagnetic resonance [116,117], nuclear magnetic resonance [118,119], ultrasonic wave propagation[120] etc. The details of the phases and transition temperatures are compiled in Table 1.2.

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Table 1.1 : Number of vibrations of each species for the point group  $T_d$  [3].

| Point group,<br>total number<br>of atoms       | Species of<br>vibration | Number of vibrations* |                           |
|--|-------------------------|-----------------------|---------------------------|
|  |                         | Non genuine           | Genuine                   |
|  |                         | T                     | R                         |
| $T_d$<br>( $N=24m+12m_d$<br>$+6m_2+4m_3+m_o$ ) | $A_1$                   |                       | $3m+2m_d+m_2+m_3$         |
|  | $A_2$                   |                       | $3m+m_d$                  |
|  | E                       |                       | $6m+3m_d+m_2+m_3$         |
|  | $F_1$                   | 1                     | $9m+4m_d+2m_2+m_3-1$      |
|  | $F_2$                   | 1                     | $9m+5m_d+3m_2+2m_3+m_o-1$ |

\*  $m$  is the number of sets of nuclei not on any element of symmetry,  $m_o$  is the number of sets of nuclei on all elements of symmetry,  $m_2$ ,  $m_3$  are the number of sets of nuclei on a two fold and three fold axis but not on any other element of symmetry that does not wholly coincide with that axis,  $m_d$  are the number of sets of nuclei on plane  $\sigma_d$  but not on any other element of symmetry.

Table 1.2 : Summary of observed phase transitions sequence in  $(\text{TM}_\text{A})_2\text{MX}_4$  compounds.\*

| Phase                    | $\text{MX}_4$ | $\text{ZnCl}_4\text{-d}_\text{O}$ | $\text{CoCl}_4\text{-d}_\text{O}$ | $\text{FeCl}_4\text{-d}_\text{O}$ | $\text{MnCl}_4\text{-d}_\text{O}$ | $\text{CuCl}_4\text{-d}_\text{O}$ | $\text{ZnCl}_4\text{-d}_{12}$ | $\text{ZnBr}_4\text{-d}_\text{O}$ | $\text{CoBr}_4\text{-d}_\text{O}$ | $\text{CuBr}_4\text{-d}_\text{O}$ |
|--------------------------|---------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Cooling Heating          |               |                                   |                                   |                                   |                                   |                                   |                               |                                   |                                   |                                   |
| I<br>(normal)            |               |                                   |                                   |                                   |                                   |                                   |                               |                                   |                                   |                                   |
| II<br>(Incom)            | 23.6          | 20.6                              | 6.9                               |                                   | 19.3                              | 27                                | 27.5                          | 24.7                              | 13.5                              | 13.8                              |
| III<br>(Com. Ferro-Ele.) | 7.0           | 8.0                               | -6.9                              |                                   | 18.7                              | 22                                | 2                             | 14.0                              |                                   | -31                               |
| II<br>(Incom)            | 2.3           |                                   | 6.3                               |                                   |                                   |                                   |                               |                                   |                                   | -36                               |
| IV<br>(Com. Elas.)       |               |                                   | 4.5                               |                                   |                                   |                                   |                               |                                   |                                   |                                   |
| III"<br>(Incom)          |               |                                   |                                   |                                   |                                   |                                   | 10.5                          |                                   |                                   |                                   |
| V                        | -10.5         | -8.1                              | -3.2                              |                                   | -6.3                              | -11                               | 4.5                           | 4.9                               |                                   |                                   |
|                          | -11.8         | -15.1                             |                                   |                                   |                                   |                                   | -1.4                          | 6.5                               |                                   |                                   |

\* All transition temperatures are in  $^\circ\text{C}$ .

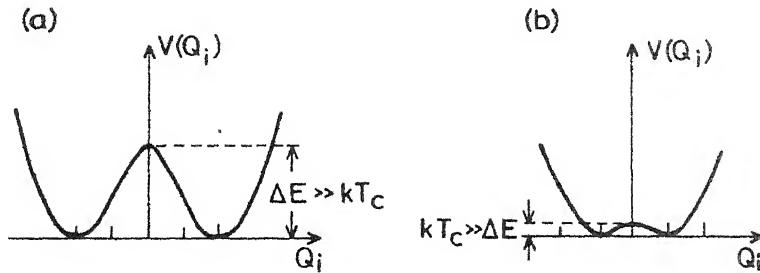


Fig.1.1 Single cell potentials in (a) order-disorder, (b) displacive structural phase transition system [36].

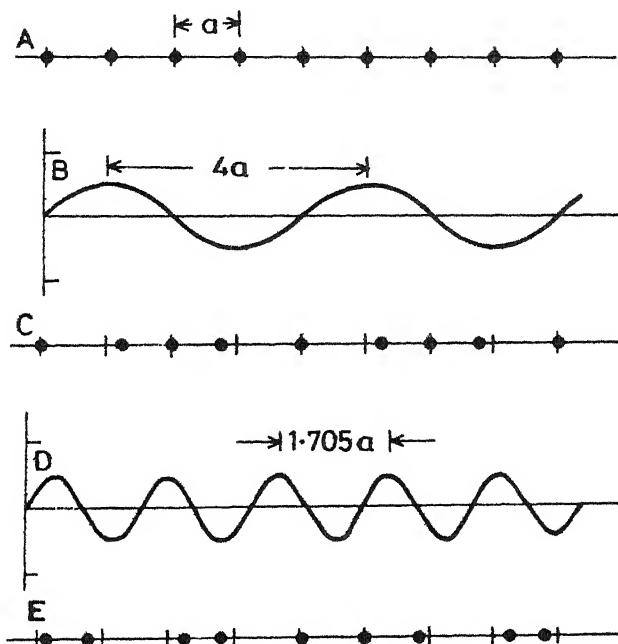


Fig.1.2 A, a uniform chain of atoms; B, a commensurable modulation; C, distorted chain which results when the modulation of B is imposed on the chain in A; D, an incommensurable modulation; E, distorted chain which results when the modulation of D is imposed on chain in A. In rows A, C and E the tick marks represent the position of the undisplaced atoms [56].

## 2. EXPERIMENTAL

This chapter briefly describes the main techniques used to record the Raman and infrared spectra at ambient, lower and higher temperatures. Emphasis is given on the techniques employed rather than on the description of the instruments used. The method used to resolve an observed contour of overlapping bands is also outlined.

### 2.1 SAMPLE PREPARATION

Commercially available AR-grade tetramethyl ammonium halides were used to record the spectra. Normal tetramethyl ammonium halides were obtained from SISCO, Bombay. Perdeuterated tetramethyl ammonium chloride was obtained from MSD, Canada. Selectively deuterated tetramethyl ammonium iodides (TMAI-d<sub>n</sub>; n = 1, 3, 9, 10, 11 and 12) were obtained from Isocommerz GmbH, German Democratic Republic. Tetramethyl ammonium chlorides (normal and perdeuterated) are highly hygroscopic. So they were dried under vacuum at least for 8 hours at room temperature before use.

Single crystals of normal tetramethyl ammonium tetrachlorozincate were grown by slow evaporation at room temperature from an aqueous solution containing stoichiometric proportions of TMACl-d<sub>0</sub> and ZnCl<sub>2</sub> [1]. The crystals were properly cut and polished with morphology suggested by Wada et al. [2]. The steps are shown in Fig. 2.1.

## 2.2 RAMAN SPECTRA

The Raman data were obtained with a Spex model 1403 Ramalog spectrophotometer, using a 5 watt Spectra Physics model 165-09 argon ion laser as exciting source. A block diagram of the experimental set up is shown in Fig. 2.2.

To obtain stabilized three phase 203 volts for the laser power supply the three phase mains voltage is first stabilized to 400 volts by a 20 KVA voltage stabilizer and then converted to 203 volts by a 12.6 KVA power transformer. The laser head and its power supply are cooled by distilled water circulated in a closed loop and maintained at a temperature of 20 °C by the HX-500 chilling plant obtained from Neslab. The heat of the chilling plant is dissipated through tap water.

The optical diagram of the set up for Raman studies is shown in Fig. 2.3. The 514.5 nm Ar<sup>+</sup> laser beam in light control mode is used for excitation of the samples. The laser beam passes through the lasermate which filters out the plasma lines. Then it enters the UVISIR illuminator, where a low focal length fused silica condenser lens focusses the laser beam of 1.5 mm diameter to a spot of 10  $\mu$ m diameter on the sample. An elliptical mirror collects the scattered radiations and focusses it on the entrance slit of the monochromator. The outcoming radiation falls onto a thermoelectrically cooled C-31034 photomultiplier tube used as the detector. The signal is analysed by the Spex photon counting system DPC-2 and the spectrum is recorded on a linear chart recorder.

To study the polarization of Raman bands a polarizer (analyser) is placed before the elliptical mirror and a scrambler is placed before the entrance slit which converts the plane polarized light to circularly polarized light. The plane of polarization of the laser beam can be rotated by  $90^\circ$ , keeping a polarization rotator before the lasermate.

#### 2.2.1 Spectra at Room Temperature

The following principal methods were used to obtain the Raman spectra :

##### (i) For solutions

The solution was taken in a cylindrical quartz cell with a flat bottom. The laser beam entered from the bottom and the scattered light was collected from the curved sides of the cell.

##### (ii) For polycrystalline samples

###### (a) Capillary method

The finely ground sample was filled in a quartz capillary, which was mounted on a stand in the sample compartment. It is the most widely used technique for colourless samples and requires a very small quantity of the sample.

###### (b) Rotating sample method

Some compounds (mostly coloured ones) strongly absorb the incident laser beam and get decomposed/dehydrated due to

localized heating. In such cases a pellet of the pure sample was mounted on a rotating sample holder. The rotation gives relative motion between the sample and laser beam, and avoids local heating.

(iii) For single crystals

A properly cut and polished crystal was mounted on a goniometer and the Raman scattering was observed in  $90^\circ$  geometry. A component of the scattering tensor, say  $\alpha_{xy}$ , is determined experimentally by arranging the crystal geometry such that the incident light is polarized in X-direction and the Y-component of the scattered light is allowed to enter the monochromator. The polarizability character of a particular spectrum and the geometry in which it was recorded can be represented by notations like  $z(xz)y$  [3,4] (see Fig. 2.4), where the symbols Z and Y outside the parenthesis denote the direction of propagation of the incident and scattered beams, respectively, while the symbols X and Z inside the parenthesis indicate the polarization characters of the incident and the scattered light, respectively.

#### 2.2.2 Spectra at Low Temperature

For low temperature Raman studies a cell shown in Fig. 2.5 has been fabricated. Typical sample holders used for different samples are also shown. Essentially the cell is a cylindrical glass dewar with the bottom parts modified. The inner jacket bottom carries a rectangular brass attachment

for the sample holder joined to the dewar with the help of a Kovar seal. The outer jacket bottom has two quartz windows, one at the bottom for the incident laser beam and the other on the cylindrical surface for the outcoming scattered radiation. Liquid nitrogen cools the brass block and hence the sample. In order to reach temperatures below the normal nitrogen boiling point, an arrangement was made for evaporation of liquid nitrogen under reduced pressure. A T-joint was attached to the inner jacket of the cell with the help of male-female joint and was driven by two rotory pumps. This system provided temperatures down to 63 K. The temperature was controlled with a 25 watts heater attached with the sample holder. A copper-constantan thermocouple, whose junction was kept in contact with the sample, was used to measure the temperature. The temperature could be controlled within  $\pm 2$  K, and measured within  $\pm 1$  K.

#### 2.2.3 Spectra at High Temperature

The Raman spectra at temperatures above the ambient temperature were recorded with a locally fabricated cell shown in Fig. 2.6. It consists of three parts : (i) the heating block, (ii) the sample holders and (iii) the temperature controller.

The heating block ( $18 \times 18 \times 38 \text{ mm}^3$ ) with a 8 mm diameter hole drilled to a depth of 28 mm (to insert the sample holder) is made of brass. This is heated from three sides by 25 watts

heaters fitted into properly created grooves. On the bottom and the fourth side two conical holes are drilled to admit the exciting radiation and collect the scattered radiation, respectively. The whole system is mounted on a spex three-way motion platform to permit alignment of the sample. Different types of sample holders for studying liquid, polycrystalline (even hygroscopic) and single crystal samples are shown in Fig. 2.6, and need no description.

A Cu-constantan thermocouple kept in contact with the sample measures the temperature. Another Cu-constantan thermocouple is connected to a relay for controlling the temperature; junction of this thermocouple is attached to the heating block in order to provide quicker response due to its higher heat capacity and conductivity. Temperatures upto 600 K, controllable upto  $\pm 1$  K, could be achieved with this system.

### 2.3 INFRARED SPECTRA

The infrared spectra were recorded on Perkin Elmer-580 spectrophotometer with dry air purging system and covering the range  $4000-180\text{ cm}^{-1}$ . Its details are well described elsewhere [5]. The spectrum of polystyrene was used for calibration of the frequency scale.

For solution state spectra a drop of the aqueous solution was pressed between two AgBr windows, thus giving a thin absorbing layer. The infrared spectra of polycrystalline

sample were recorded in KBr pellets and nujol mulls. For temperature dependence studies the samples were kept in a Specac variable temperature cell (Fig. 2.7). The temperature of the sample could be stabilized to within  $\pm 2$  K in the range 77 to 523 K.

#### 2.4 RESOLUTION OF THE OVERLAPPING BANDS

There are many instances in which two or more neighbouring bands overlap considerably to give a contour. Although unique resolution in such contours is fraught with many uncertainties, it is useful to extract some information by resolving such a contour by geometrical drawing. The component bands in an experimental band contour are expected to be Voigt like combinations of Lorentzian and Gaussian curves [6]. However, if the actual band width of each component is substantially larger than the instrumental slit width, the Lorentzian shape alone gives a reasonably good fit, especially when one does not look far into the tails of the components. Further, in the condensed phase theoretical considerations also justify the use of Lorentzian shapes for the bands in the contour [7]. Therefore we have assumed Lorentzian shapes to resolve the overlapping bands geometrically. A Lorentzian contour  $I(\nu)$  around a band centre  $\nu_0$  is given as

$$I(\nu) = I(\nu_0) \frac{b^2}{b^2 + (\nu - \nu_0)^2} \quad (2.1)$$

where  $2b$  is the full band width at half the maximum intensity, designated as  $\Delta\nu_{1/2}$ .

Selection of a proper base line is the first step for the analysis of an overlapping band. This we did by considering the general base well beyond the band, and allowing for the contribution of the tails. Having chosen the base line, a linear absorbance plot was drawn for the observed contour. It was then resolved into the minimum number of Lorentzian components as justified by the peaks, shoulders and distinct bulges in the contour. Some initial  $I(\nu_0)$  and  $\Delta\nu_{1/2}$  parameters were chosen for the different components and the corresponding absorbance curves obtained from eq. 2.1 were plotted and added together. From the deviation between this and the observed contour new  $I(\nu_0)$  and  $\Delta\nu_{1/2}$  parameters were estimated and the process was repeated. The best fit obtained after a few iterations was used as the final result. Minor residues or deviations were ignored, since the Lorentzian shape is only an approximation. In case more than one alternative analysis gave equally good fit, that which maintained the peak positions nearer the observed humps was preferred. A component not indicated in the contour by a hump or a shoulder was introduced only in those cases where repeated Lorentzian trials otherwise failed by wide margins and there were spectral evidences too for such a component.

The inaccuracies of the derived parameters vary from one situation to another. Band positions are accurate to within  $\pm 2 \text{ cm}^{-1}$  for sharp peaks,  $\pm 5 \text{ cm}^{-1}$  for broad but distinct bands and shoulders, and  $\pm 10 \text{ cm}^{-1}$  for bulges and very weak evidences. For intensities the error level may be upto 10% in the case of envelopes with weak overlappings and upto 30% in the case of envelopes with strong overlapping.

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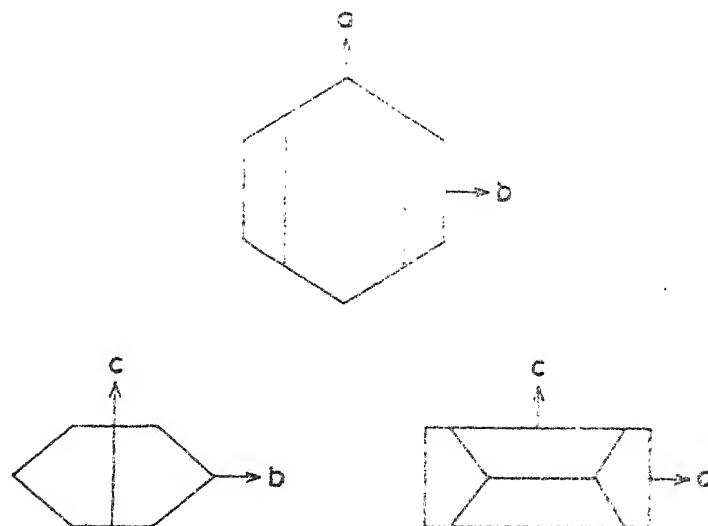


Fig. 2.1 Form of typical as grown  $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$  crystal [2].

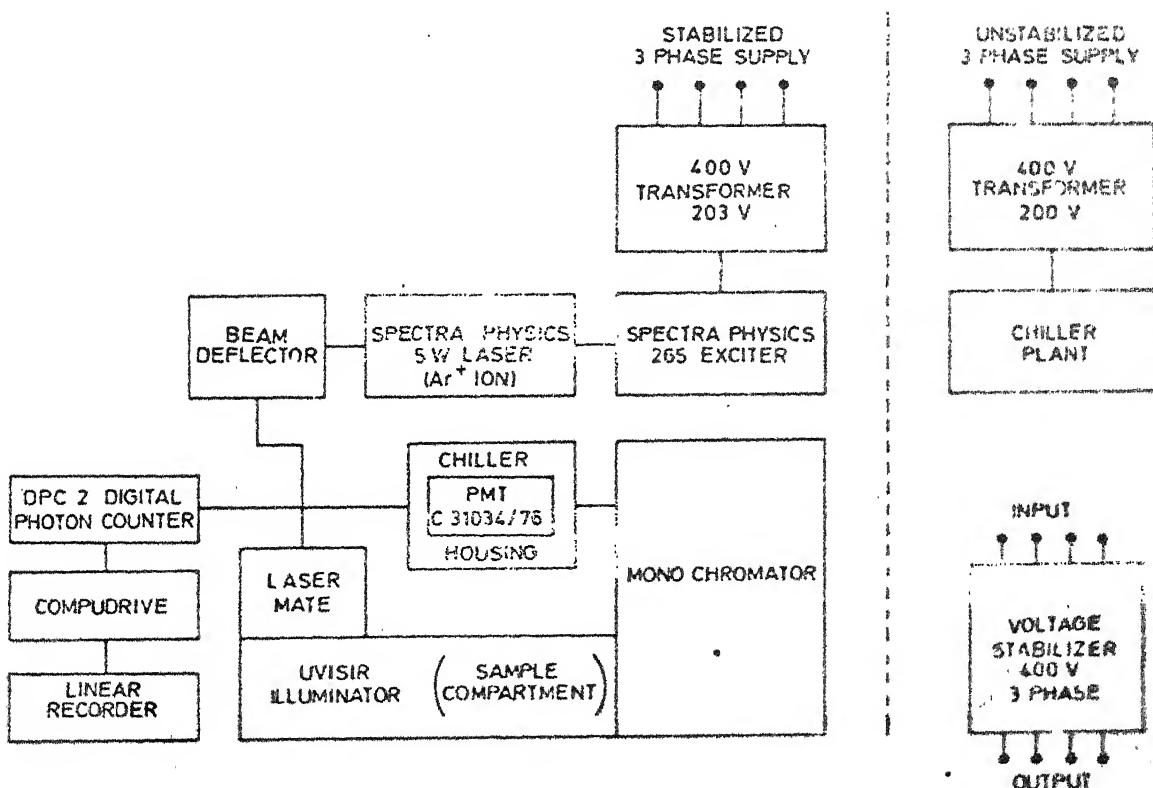


Fig. 2.2 Laser Raman spectrometer (Block diagram).

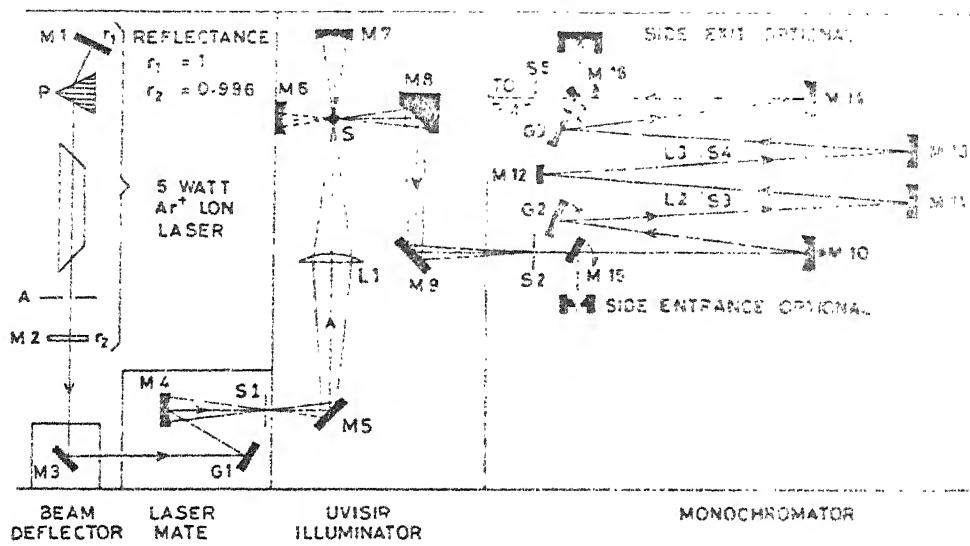


Fig. 2.3 Optical diagram of spectra physics laser and Ramalog 1403 spectrometer.

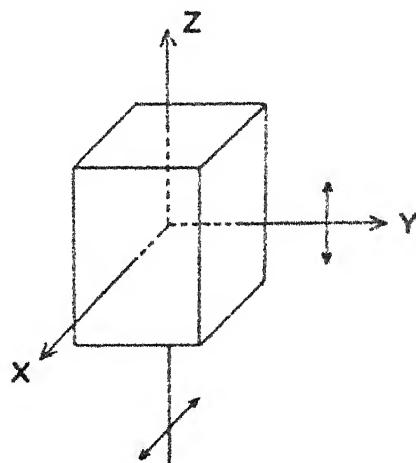
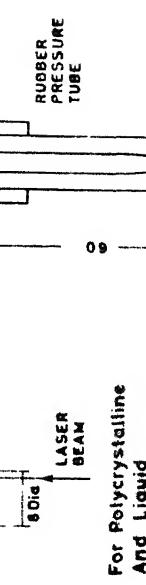
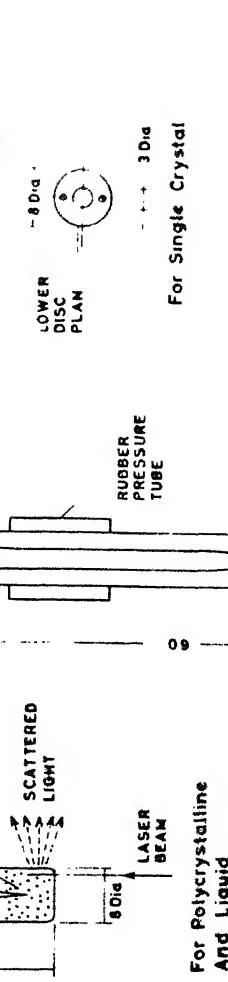
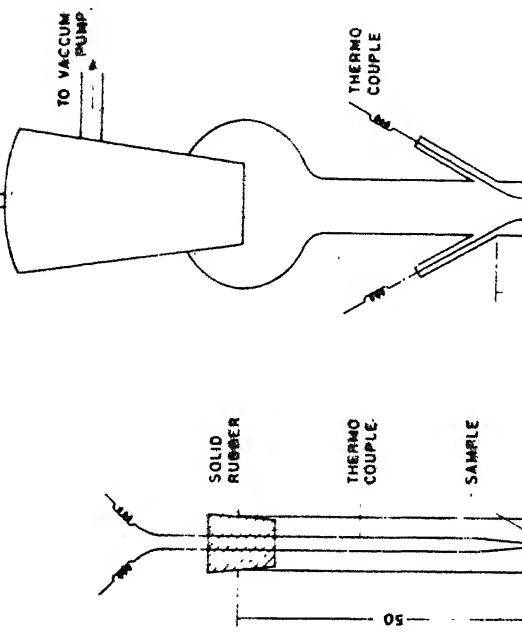
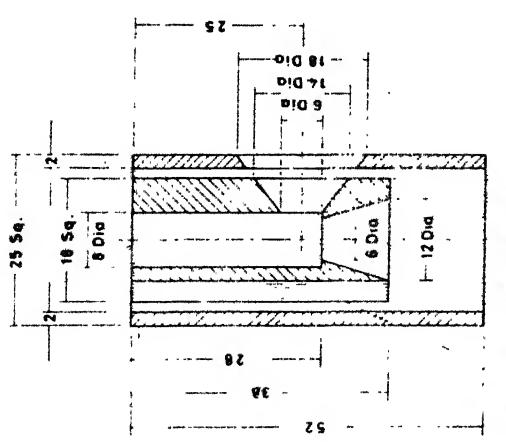
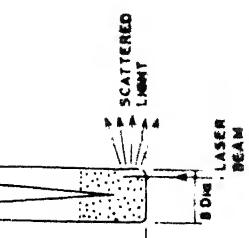


Fig. 2.4 Excitation geometry, Z(XZ)Y.

### SAMPLE HOLDERS



For Single Crystal



ALL DIMENSIONS ARE IN MM

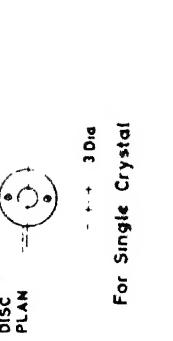
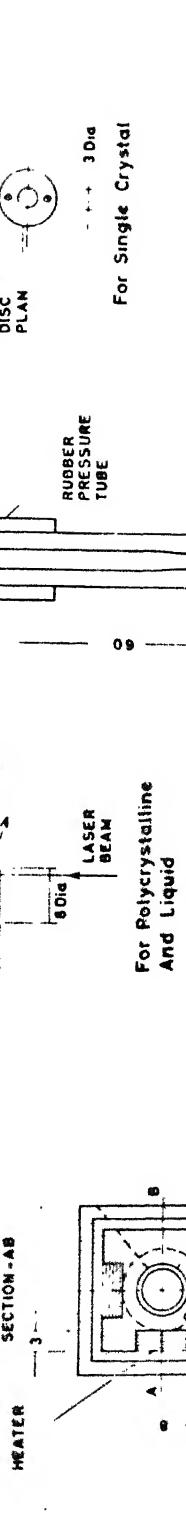
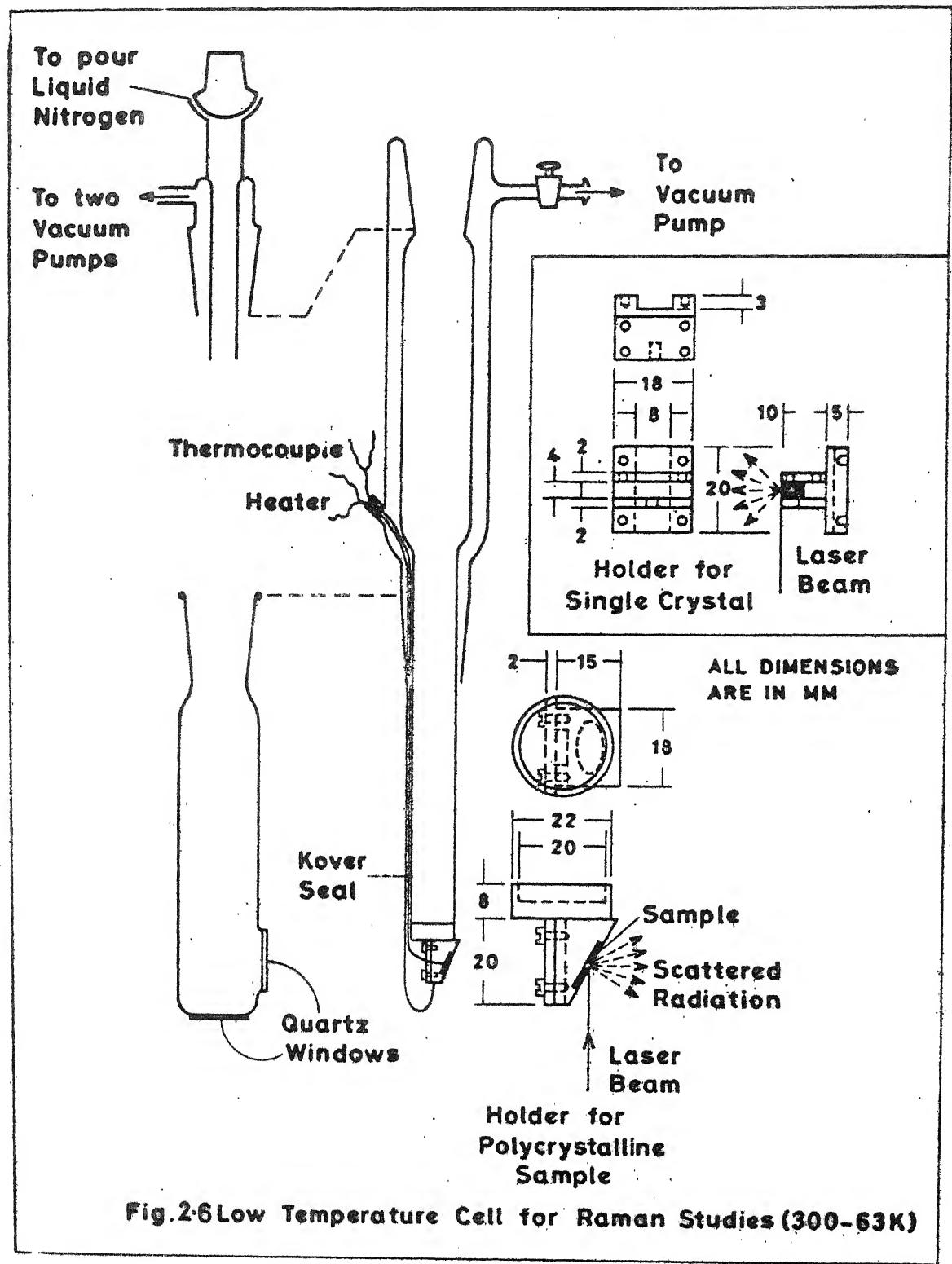


Fig. 2.5 The design of a high temperature cell with different types of sample holders for Raman Studies.



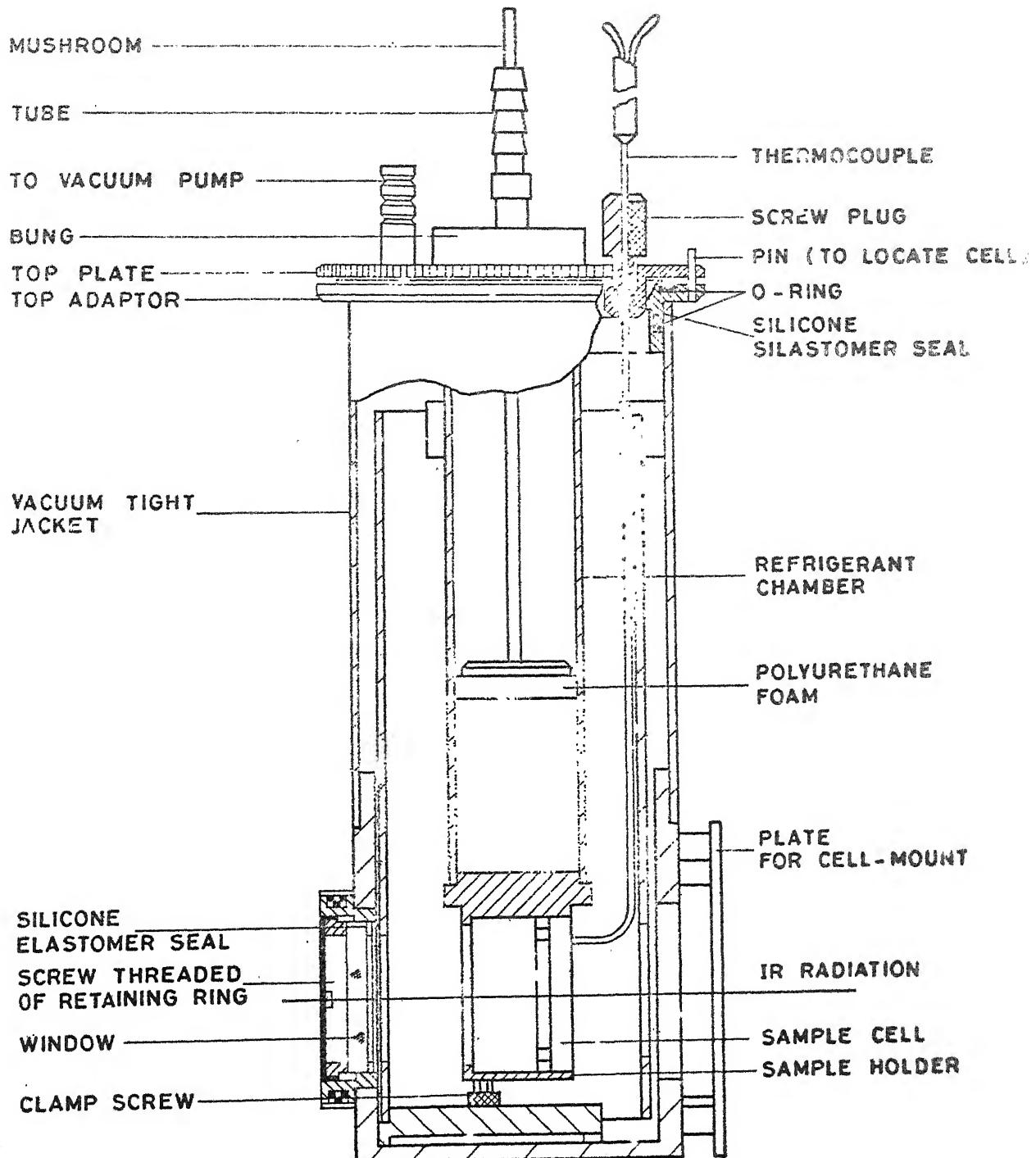


Fig. 2.7 SPECAC VARIABLE TEMPERATURE CELL

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### 3. VIBRATIONAL STUDIES AND PHASE TRANSITIONS IN NORMAL ( $d_0$ ) AND PERDEUTERATED ( $d_{12}$ ) TETRAMETHYL AMMONIUM CHLORIDES

In this chapter we present our vibrational studies (Raman and infrared) of TMACl- $d_0$  and TMACl- $d_{12}$ . We attempt to explain the three abnormally high intensity bands in the  $\text{CH}_3$  stretching region in TMACl- $d_0$  by proposing a model in which the  $T_d$  symmetry of TMA- $d_0$  ion dynamically distorts to  $C_{3v}$  [1]. We have characterized three phase transitions above liquid nitrogen temperature in TMACl- $d_0$  and one phase transition above room temperature in TMACl- $d_{12}$  [2,3].

#### 3.1 CRYSTAL STRUCTURE

The TMA halides (chloride, bromide and iodide) are isostructural at room temperature as determined by X-ray diffraction studies [4-6]. They belong to the tetragonal system with space group  $D_{4h}^7$  ( $z = 2$ ). A two dimensional view of the structure in XY plane is given in Fig. 3.1.

Vegard and Sollesnes [4] assigned the carbon atoms to the site  $C_s(8)$  of  $D_{4h}^7$ , which yields the same antiparallel arrangement of tetrahedra as in the tetragonal phase of  $\text{ND}_4\text{Br}$  [7,8]. Also the space group  $D_{4h}^7$  requires the 24 hydrogen atoms in the unit cell to be divided either into three groups of 8 equivalent hydrogen atoms each or into two groups, one

of 8 and the other of 16. Only the latter arrangement is structurally acceptable to the cation at any temperature [8]. Powder patterns of  $\text{TMACl-d}_0$  in phase II have been reported by Dufourcq et al. [9] and Pistorius and Gibson [8]. Since  $\text{TMACl-d}_0$  in phase II is known to be piezoelectric [10], it must have a non-centrosymmetric space group. The structure is shown to be rhombohedral with one formula unit per unit cell [9].

Pistorius and Gibson [8] have suggested a space group  $C_{3v}^5$  ( $z = 1$ ) using X-ray diffraction powder pattern in phase II and calculation of configurational entropy in phases III and II. In this structure the anion is located at the  $C_3$  axis of the site  $C_{3v}$ . The nitrogen atom and one carbon atom are also on the three fold axis in the  $C_{3v}$  site. The other three carbon atoms of the tetrahedron cation occupy  $C_1$  site.

In phase I the structure of  $\text{TMACl-d}_0$  has been shown to be face-centred cubic with four formula units per unit cell [9]. Pistorius and Gibson [8] have found the space group to be  $O_h^5$  ( $z = 4$ ) with  $a_0 = 9.11 \text{ \AA}$  using configurational entropy calculation and X-ray powder pattern. There are a number of possible arrangements in this space group, but in the absence of sufficiently accurate diffraction intensities it is not possible to make a definite choice [8]. Regarding phase IV Tench [11] reports that the structure is the same (tetragonal) as for the room temperature phase, i.e., phase III, the unit cell dimensions also being only marginally different.

### 3.2 GROUP THEORETICAL ANALYSIS

The TMA group retains its identity over a wide range of environmental conditions. It is, therefore, appropriate to take TMA as a distinct group in any group theoretical analysis under the site symmetry approach. In phase II ( $C_{3v}^5$ ,  $Z = 1$ ) the total number of modes, 54, for a unit cell could be distributed as six translatory phonons (including three acoustic phonons), three rotatory modes and forty five internal vibrations of the TMA ion. Two types of configurations, eclipsed and staggered [12,13], are possible for the TMA under the point group symmetry  $T_d$ . But the distributions of vibrational modes of TMA ion are the same for both the configurations. This is given in Table 3.2 :

$$\Gamma_{\text{vib}}^{\text{TMA}} = 3A_1 + A_2 + 4E + 4F_1 + 7F_2 \quad (3.1)$$

Young et al. [14] have pointed out that it is somewhat arbitrary to define one observed frequency as carbon-hydrogen frequency and another as that of  $C_4N$ , because in TMA ion the central atom (N) and the methyl carbon atoms are strongly bonded. Yet we present an approximate description of the observed modes in terms of vibrations of methyl group and the  $C_4N$  skeleton as given in Table 3.3. We have adopted the standard Herzberg's notations to denote the vibrations [15].

In other phases the distribution of total number of modes can be obtained from that of phase II ( $Z = 1$ ) by multiplying it with the number of formula units per unit

cell ( $z$ ) in the desired phase ( $z = 4$  for phase I and  $z = 2$  for phase III). Table 3.4 illustrates the correlations of the species of factor groups  $C_{3v}$  and  $D_{4h}$  for phases II and III, respectively, through the species of their respective sites. The internal modes of TMA ion in phase II (45 in total) and phase III (90 in total) are distributed as follows

$$\sum_{vib}^{II} = 10A_1(R, IR) + 5A_2 + 15E(R, IR) \quad (3.2)$$

$$\begin{aligned} \sum_{vib}^{III} = & 7A_{1g}(R) + 4A_{2g} + 7B_{1g}(R) + 5B_{2g}(R) + 11E_g(R) \\ & + 5A_{1u} + 7A_{2u}(IR) + 4B_{1u} + 7B_{2u} + 11E_u(IR) \quad (3.3) \end{aligned}$$

For phase IV and V no structural data are available.

The space group for phase I has been suggested to be  $O_h^5$  ( $z = 4$ ) [8], but no possible site symmetry corresponding to  $z = 4$  is available [16]. Therefore a group theoretical analysis for these phases could not be carried out.

### 3.3 VIBRATIONAL SPECTRA OF TMACl-d<sub>6</sub> IN AQUEOUS SOLUTIONS

The observed Raman spectra of an aqueous solution of TMACl-d<sub>6</sub> (7 M) for both parallel and perpendicular polarizations are shown in Fig. 3.2. The normal Raman spectra with variation of concentration are shown in Fig. 3.3. The IR spectrum of an aqueous solution of TMACl-d<sub>6</sub> is given in Fig. 3.4. The observed band positions with half widths and relative integrated intensities are given in Table 3.5. IR

and Raman data of Berg [17] for TMACl-d<sub>12</sub> are also given in Table 3.5 for comparison and completeness.

The modes of C<sub>4</sub>N skeleton have been assigned without controversy with the help of polarization data and exclusion principle [18] in Raman and IR spectra. A weak shoulder at 736 cm<sup>-1</sup> in the Raman spectrum (0.5 M) towards the lower frequency side of the intense band  $\nu_3(A_1)$  is assigned as the overtone of  $\nu_{19}(F_2)$ . The band at 920 cm<sup>-1</sup> in the spectrum is assigned as the overtone of  $\nu_{18}(F_2)$ .

The CH<sub>3</sub> symmetric bending mode  $\nu_2(A_1)$  has not been ascertained experimentally in the Raman spectra of the compounds containing TMA-d<sub>0</sub>. A polarized band in the Raman spectra of TMACl-d<sub>12</sub> at 1144 cm<sup>-1</sup> is observed in the region free from the other bands [17]. The position of  $\nu_2(A_1)$  in TMACl-d<sub>0</sub> is estimated to be  $\sim 1450$  cm<sup>-1</sup> on the basis of isotopic shift calculations. But it could neither be detected by extracting the pure isotopic scattering intensity from the difference  $I_{11} - \frac{4}{3}I_1$  nor from a plot between depolarization ratio versus wavenumber which should give a dip at the position of  $\nu_2(A_1)$  mode [19]. Thus for TMACl-d<sub>0</sub> the in-phase bending mode  $\nu_2(A_1)$  must be of negligible intensity, whereas it appears as a sharp band of appreciable intensity in the spectrum of TMACl-d<sub>12</sub>. Kabisch and Möbius [19] have shown theoretically that  $\nu_2(A_1)$  in TMACl-d<sub>12</sub> gets intensity due to mixing of wavefunctions of C<sub>4</sub>N and CD<sub>3</sub> groups, whereas in TMACl-d<sub>0</sub> its intensity is very low. Taylor et al. [20] have calculated with the help of bond

polarizability theory that the intensities of  $\nu_2(A_1)$  in the normal and deuterated tetramethyl methanes are in ratio 0.7:1.2. Young et al. [14] have pointed out that the methyl group deformation and rocking modes of  $F_2$  species  $\nu_{15}(F_2)$ ,  $\nu_{16}(F_2)$  and  $\nu_{17}(F_2)$  resonate with the  $C_4N$  asymmetric stretch,  $\nu_{18}(F_2)$  and get pushed up. Accordingly, one may expect resonance between  $CD_3$  symmetric deformation  $\nu_2(A_1)$  and  $C_4N$  symmetric stretch  $\nu_3(A_1)$  in  $TMACl-d_{12}$  which are more close in  $TMACl-d_{12}$  than in  $TMACl-d_0$ . Thus  $\nu_2(A_1)$  mode would appear more intense in  $TMACl-d_{12}$  than in  $TMACl-d_0$ .

The methyl symmetric stretching mode,  $\nu_1(A_1)$  is quite difficult to assign due to appearance of a number of intense polarized bands observed in the stretching region. The assignments are based on two alternative considerations : (i) Fermi resonance and anharmonicity and (ii) dynamic distortion of the  $C_4N$  skeleton. It is noted that the calculated mechanical anharmonicities vary marginally on going from the dilute to the concentrated solution while the relative intensities change drastically.

### 3.3.1 Fermi-resonance and Anharmonicity

Our assignments, shown in column 8 of Table 3.5 are analogous to those proposed by Kabisch and Klose [21]. The moderate intense band at  $2826\text{ cm}^{-1}$  (in 0.5 M solution) shows the largest mechanical anharmonicity and its intensity is about an order of magnitude smaller than that of the other

strong polarized bands. This band has been attributed to an overtone of the  $\nu_{16}(F_2)$  mode. Similarly the other very weak bands at 2920 and  $2905\text{ cm}^{-1}$  (in 0.5 M solution), with less anharmonicities, are assigned to a combination and an overtone respectively. The depolarized band at  $3043\text{ cm}^{-1}$  and the polarized band at  $2991\text{ cm}^{-1}$  can safely be assigned to the  $\text{CH}_3$  asymmetric and the  $\text{CH}_3$  symmetric stretching modes respectively. The polarized band at  $2966\text{ cm}^{-1}$  can also be justified as the allowed  $A_1$  component of the overtone of  $\nu_{15}(F_2)$  mode. The other polarized band at  $2933\text{ cm}^{-1}$  cannot be assigned as the combination of the  $\nu_6(E)$  and the  $\nu_{15}(F_2)$  modes.

In general, due to Fermi-resonance, the resonating band which is nearer to the fundamental gains more intensity than the band farther from it. Neither the Fermi-resonance nor the electrical anharmonicity consideration can alone explain the observed intensity distribution in this region and its variation with concentration. The Fermi-resonance combined with the electrical anharmonicity (coupled with mechanical anharmonicity) may explain the observed abnormal intensity distribution. One may argue that the band at  $2933\text{ cm}^{-1}$  may have more electrical anharmonicity (as would be expected on the basis of higher mechanical anharmonicity) than the band at  $2966\text{ cm}^{-1}$ , making it ( $2933\text{ cm}^{-1}$  band) more intense under Fermi-resonance than the band at  $2966\text{ cm}^{-1}$  which is closer to the fundamental at  $2991\text{ cm}^{-1}$ . However, this argument is untenable for the following reasons :

- (i) The fundamental requirement for Fermi-resonance is that the levels involved must have the same symmetry [15]. The selection rules show that the combination of  $\nu_6(E)$  and  $\nu_{15}(F_2)$  produces levels of symmetry species  $F_1$  and  $F_2$  which cannot resonate with  $\text{CH}_3$  symmetric stretching mode of symmetry species  $A_1$ .
- (ii) The intensity of the resonating band(s) can never exceed the intensity of the fundamental band, unless electrical anharmonicity is a dominating factor, which is seldom observed in Raman spectra.
- (iii) It is observed that on varying the concentration, the intensities of the resonating bands change drastically whereas the band positions remain almost unchanged. This is also not observed in Fermi-resonance especially when the positions of fundamental bands remain unchanged. Thus the intense and the polarized band at  $2933 \text{ cm}^{-1}$  cannot unambiguously be assigned to the combination of the  $\nu_6(E)$  and the  $\nu_{15}(F_2)$  modes. Therefore an alternative explanation of the three strong polarized and intense bands may be searched in the dynamic distortion of the  $\text{C}_4\text{N}$  skeleton.

### 3.3.2 Dynamic Distortion of the $\text{C}_4\text{N}$ Skeleton

The totally symmetric  $\text{CH}_3$  stretching motions of the four  $\text{CH}_3$  groups in TMA ion could result in three specific configurations consistent with the internal vibrations of

$C_4N$  skeleton as shown in Fig. 3.5. In the first configuration (Fig. 3.5a) all the C-atoms vibrate in-phase along C-N bonds. In this case the  $T_d$  symmetry of the  $C_4N$  skeleton is maintained even dynamically. This situation corresponds to  $\nu_1$  mode of species  $A_1$  for the skeleton and yields one totally symmetric polarized  $CH_3$  stretching vibration ( $A_1$ ).

In the second configuration, three C-atoms vibrate in-phase and one out-of-phase and vice versa along C-N bonds as shown in Fig. 3.5b. In this case the  $T_d$  symmetry of  $C_4N$  skeleton is distorted to  $C_{3v}$  dynamically corresponding to  $\nu_3(F_2)$  mode for the skeleton ( $T_d$ ) and yields under  $C_{3v}$  one totally symmetric polarized  $CH_3$  stretching mode ( $A_1$ ) and another asymmetric depolarized  $CH_3$  stretching mode ( $E$ ).

In the third configuration, three C-atoms vibrate in-phase perpendicular to C-N bonds and one along the C-N bond as shown in Fig. 3.5c. In this case, too, the  $T_d$  symmetry of  $C_4N$  skeleton is distorted to  $C_{3v}$  dynamically and the situation, corresponding to  $\nu_4(F_2)$  mode for the skeleton ( $T_d$ ), yields one totally symmetric polarized  $CH_3$  stretching mode ( $A_1$ ) and another asymmetric depolarized  $CH_3$  stretching mode ( $E$ ).

There are two more possible configurations with two asymmetric depolarized  $CH_3$  stretching modes corresponding to the vibrations of the  $C_4N$  skeleton of species  $E$  and  $F_1$ . It can, therefore, be concluded that three totally symmetric polarized C-H stretching bands must arise from dynamic distortion of  $C_4N$  skeleton and coupling between the four  $CH_3$

groups. That would explain the three observed  $A_1$  modes in  $\text{CH}_3$  stretching region.

The four  $\text{CH}_3$  asymmetric stretches may appear at the same frequency giving thereby a single depolarized band at  $3043 \text{ cm}^{-1}$  (in 0.5 M solution). The larger half-width of this band and its shift with concentration may also corroborate the presence of more than one unresolved bands under the combined envelope.

A correlation of isolated  $\text{CH}_3$  stretching vibrations ( $C_{3v}$  point groups) with those of TMA under  $T_d$  and  $C_{3v}$  point groups is given in Table 3.6. Under the group  $T_d$  in TMA the C-H symmetric stretching ( $A_1$ ) vibrations of four isolated  $\text{CH}_3$  groups produce a totally symmetric species  $A_1$  and a triply degenerate species  $F_2$ . Likewise, the four isolated  $\text{CH}_3$  asymmetric stretching modes ( $E$ ) under  $C_{3v}$  produce a doubly degenerate  $E$  species and two triply degenerate species  $F_1$  and  $F_2$  under  $T_d$  point group as shown in the second column of Table 3.6. As a result under the point group  $T_d$  one expects in the  $\text{CH}_3$  stretching region four Raman active bands out of which only one should exhibit totally symmetric and polarized ( $A_1$ ) character.

If the  $\text{C}_4\text{N}$  group of TMA acquires a  $C_{3v}$  symmetry even dynamically (e.g., this could be the case during its  $\nu_3$  vibration as discussed later and shown in Fig. 3.5) the situation gets changed as illustrated in the third column of Table 3.6. It is evident that one would expect a maximum of three totally

symmetric polarized ( $A_1$ )  $\text{CH}_3$  stretching bands along with four doubly degenerate ( $E$ ) depolarized C-H stretching modes. This situation will be applicable to the solutions where the crystalline field effects would be missing.

To get rid of the difficulty in assigning the band at  $2933 \text{ cm}^{-1}$  as combination of  $\nu_6(E)$  and  $\nu_{15}(F_2)$  Kabisch and Mobius [22] have pointed out that in the  $\text{CH}_3$  stretching region a number of overtones of  $\nu_2(A_1)$ ,  $\nu_7(E)$ ,  $\nu_{11}(F_1)$ ,  $\nu_{16}(F_2)$  and  $\nu_{17}(F_2)$  are falling, which may resonate with  $\nu_1(A_1)$ . The appearance of only one strong band in  $\text{CH}_3$  symmetric stretching region in Raman spectra of polycrystalline TMA halides can also not be explained on the basis of dynamic distortion of  $\text{C}_4\text{N}$  skeleton.

### 3.4 CHARACTERISTIC RAMAN SPECTRA OF $\text{TMACl-d}_6$ IN THE FOUR PHASES ABOVE LIQUID NITROGEN TEMPERATURE AND THEIR ASSIGNMENTS

The relevant portions of the observed Raman spectra of  $\text{TMACl-d}_6$  in phases I (at 540 K), II (at 393 K and 300 K on cooling under vacuum), III (at 300 K) and IV (at 90 K) are depicted in Fig. 3.6. The observed band positions with half widths and relative integrated intensities are given in Table 3.7. The vibrational assignments of the observed bands are suggested under the undistorted point group symmetry  $T_d$  of tetramethyl ammonium ion and without taking into account the splitting due to lowering of symmetry on account of the crystal field.

### 3.4.1 Phase I

For  $\text{TMACl-d}_0$ , Pistorius and Gibson [8] have suggested the space group for the phase I to be  $O_h^5$  ( $Z = 4$ ). The possible site symmetries for space group  $O_h^5$  are  $2O_h(1)$ ,  $T_d(2)$ ,  $D_{2h}(6)$ ,  $C_{4v}(6)$ ,  $C_{3v}(8)$ ,  $3C_{2v}(12)$ ,  $2C_s(24)$  and  $C_1(48)$  [16]. So there is no possible site symmetry in this space group that can contain four symmetry points. According to Dufourcq et al. [9] the cations are at two  $T_d$  sites. If it is true, the Raman spectra of  $\text{TMACl-d}_0$  in phase I must closely resemble with the aqueous solution spectra as observed by Kabisch [22] in  $[(\text{CH}_3)_4\text{N}]_2\text{SnCl}_6$ . But in phase I the intensities of all the bands reduce to nearly zero. So it seems that either  $\text{TMACl-d}_0$  does not have space group  $O_h^5$  ( $Z = 4$ ) in phase I or due to some other effects intensities of the bands are suddenly reduced to zero. Amongst possible reasons suggested are very low activation energy for  $\text{CH}_3$  librations [8] and occurrence of ionic diffusion in this phase [10].

### 3.4.2 Phase II

The Raman spectrum of  $\text{TMACl-d}_0$  in this phase at 393 K below  $1300 \text{ cm}^{-1}$  is similar to the aqueous solution spectrum except for the occurrence of some additional details. The asymmetric stretching mode of  $\text{C}_4\text{N}$ ,  $\nu_{18}(F_2)$  appears as a doublet in phase II which is clearly resolved on cooling the sample to room temperature in the same phase as shown in Fig. 3.6. It is consistent with the group theoretical

splitting. A band at  $1068 \text{ cm}^{-1}$ , appearing in phase II, gains intensity on cooling the sample to room temperature in the same phase. The band is assigned to  $\text{CH}_3$  rocking,  $\nu_{11}(\text{F}_1)$ . Kabisch [22] observed a very weak band at  $1081 \text{ cm}^{-1}$  in phase III and assigned it to this mode.

In the Raman spectra of  $\text{TMACl-d}_0$  above  $1300 \text{ cm}^{-1}$  we get two strong bands at  $1403$  and  $1462 \text{ cm}^{-1}$  in  $\text{CH}_3$  deformation region and two strong bands at  $2946$  and  $3017 \text{ cm}^{-1}$  in the  $\text{CH}_3$  stretching region. The band at  $3017 \text{ cm}^{-1}$  again splits into two components at  $3014$  and  $3028 \text{ cm}^{-1}$  on cooling the sample in the same phase.

Table 3.8 is an illustration and extension of Table 3.4 for the  $\text{CH}_3$  modes. For isolated  $\text{CH}_3$  group having  $\text{C}_{3v}$  symmetry, group theoretically the stretching (or deformation) modes produce one vibration each of species  $\text{A}_1$  and  $\text{E}$  as shown in column 1 of Table 3.8. The four symmetric stretches (or deformations) of species  $\text{A}_1$  for the four  $\text{CH}_3$  groups in TMA ion under molecular symmetry  $\text{T}_d$  produce the species  $\text{A}_1+\text{F}_2$ , and the corresponding modes are denoted as  $\nu_1$  and  $\nu_{14}$  for stretches ( $\nu_2$  and  $\nu_{16}$  for deformation). Likewise the asymmetric stretches (or deformations) of species  $\text{E}$  are distributed as  $\text{E}+\text{F}_1+\text{F}_2$ , and the corresponding modes are denoted as  $\nu_5$ ,  $\nu_9$  and  $\nu_{13}$  for stretches ( $\nu_6$ ,  $\nu_{10}$  and  $\nu_{15}$  for deformations) as given in Table 3.8. As given in column 5 of Table 3.8, the four symmetric ( $\text{A}_1$ ) and four asymmetric ( $\text{E}$ ) stretches (or deformations) are further split as the bands of species  $2\text{A}_1+\text{E}$  and  $\text{A}_1+\text{A}_2+3\text{E}$  under the factor group  $\text{C}_{3v}$  (through the site  $\text{C}_{3v}$ ). Thus all the  $\text{CH}_3$

stretches (or deformations) may split into seven ( $3A_1+4E$ ) Raman active components in phase II as given in last row of Table 3.8.  $A_2$  being inactive both in IR and R. Experimentally two strong bands in the deformation (or stretching) region are observed in the Raman spectra in phase II which are identical to the Raman spectra of isolated  $CH_3$  group. So it is appropriate to assign the bands at 1403 and  $1462\text{ cm}^{-1}$  as  $CH_3$  symmetric deformation and  $CH_3$  asymmetric deformation, respectively. Similarly in the  $CH_3$  stretching region the bands at 2946 and  $3017\text{ cm}^{-1}$  are assigned as  $CH_3$  symmetric stretch and  $CH_3$  asymmetric stretch, respectively. The splitting of  $3017\text{ cm}^{-1}$  may be due to correlation field as expected.

### 3.4.3 Phase III (RT phase)

The assignments of all the fundamentals of TMA ions for the room temperature phase III below  $1300\text{ cm}^{-1}$  are identical to those made by Kabisch [22]. In the  $CH_3$  deformation region,  $1350-1500\text{ cm}^{-1}$ , as already explained and given in Table 3.8, five bands  $\nu_2(A_1)$ ,  $\nu_{16}(F_2)$ ,  $\nu_6(E)$ ,  $\nu_{10}(F_1)$  and  $\nu_{15}(F_2)$  are group theoretically expected under the point group symmetry  $T_d$  for free TMA ion. The splittings of the bands in phase III under the factor group  $D_{4h}$  through the site  $D_{2d}$  are given in the last column of Table 3.8. In the Raman spectra of  $TMACl-d_0$  we get five bands at 1398, 1402, 1454, 1477 and  $1483\text{ cm}^{-1}$ . The doublet with components at 1398 and  $1402\text{ cm}^{-1}$  (which splits into triplet with components at 1392, 1399 and  $1407\text{ cm}^{-1}$  in phase

IV) is assigned as  $\nu_{16}(F_2)$ , consistent with group theoretical analysis. The bands of species  $F_2$  are expected to split into two Raman active ( $B_{1g}$  and  $E_g$ ) components for room temperature phase III. It is observed that most of the bands of species  $F_2$  in phase IV split into three components. Thus the bands at  $1477$  and  $1483\text{ cm}^{-1}$ , assigned as  $\nu_{15}(F_2)$  in phase III, also split into three components ( $1474$ ,  $1479$  and  $1486\text{ cm}^{-1}$ ) in phase IV. The band at  $1454\text{ cm}^{-1}$  could be assigned either to  $\nu_2(A_1)$  or to  $\nu_6(E)$ . However, it has been observed that in  $\text{CH}_3$  and  $\text{C}_4\text{N}$  stretching regions of TMA ion the intensities of the bands corresponding to symmetric species  $A_1$  are diminished with respect to the corresponding asymmetric bands in going from solution to polycrystalline state and  $\nu_2(A_1)$  could not be observed in Raman spectra of aqueous solution of  $\text{TMACl-d}_6$ . Therefore the band at  $1454\text{ cm}^{-1}$  has been assigned to  $\nu_6(E)$ . This band can, however, have some minor contribution due to  $\nu_2(A_1)$  as expected by spectra of deuterated TMA ion [17]. The band of species  $F_1$  under  $T_d$  is Raman inactive, so the band of species  $E_g$  arising from  $\nu_9(F_1)$  may be too weak to identify in polycrystalline  $\text{TMACl-d}_6$  in phase III.

#### 3.4.4 Phase IV

Pistorius and Gibson [8] have suggested that the lattice in this phase is tetragonal with lattice constants close to those of the room temperature phase III. No structural data are available for this phase. As mentioned

earlier, it is observed that most of the bands of species  $F_2$  split into three components in the Raman spectra of  $\text{TMACl-d}_0$  in this phase.

It can be expected that on lowering the temperature (III  $\rightarrow$  IV) the inversion symmetry in phase III is lost and therefore the lattice goes to a space group lower than  $D_{4h}^7$ . The most probable tetragonal space groups having four fold symmetry without inversion would be anyone from  $D_4^1$ ,  $D_4^2$ ,  $D_4^3$ ....  $D_4^{10}$ . However  $D_4^1$  and  $D_4^9$  are the only space groups which do not possess screw symmetry, thus resembling the  $D_{4h}^7$  group as far as screw symmetry is concerned. If one assumes that the primitive cell is preserved on lowering the temperature, the space group for phase IV will be  $D_4^1$  ( $z = 2$ ). Under this situation the bands of species  $F_2$  are expected to split into three Raman active components, which is actually observed in phase IV.

### 3.5 INFRARED SPECTRA OF $\text{TMACl-d}_0$

The IR spectra of  $\text{TMACl-d}_0$  in an aqueous solution kept between  $\text{AgCl}$  windows and in the polycrystalline form in  $\text{KBr}$  pellet at 300 and 90 K are shown in Fig. 3.4. The vibrational assignments are given in Table 3.5 and Table 3.7 for aqueous solution spectra and for polycrystalline spectra, respectively. The assignments are similar to those proposed by Bottger and Geddes [23] except for some details. The IR data of  $\text{TMACl-d}_{12}$

are also given in the tables for comparison and completeness.

The  $\text{CH}_3$  asymmetric stretching mode  $\nu_{13}(\text{F}_2)$  shows only one component at  $3020 \text{ cm}^{-1}$  in IR spectra of polycrystalline  $\text{TMACl-d}_0$  at 300 K. On cooling the sample to liquid nitrogen temperature (90 K), it splits into components at 3017 and  $3023 \text{ cm}^{-1}$ . The splitting may be due to correlation field as expected from group theoretical analysis.

In the  $\text{C}_4\text{N}$ -asymmetric stretching region three bands are observed at 920, 948 and  $958 \text{ cm}^{-1}$  in the IR spectra at 300 K. The bands at 948 and  $958 \text{ cm}^{-1}$  are assigned to the components of  $\text{C}_4\text{N}$ -asymmetric stretching mode  $\nu_{18}(\text{F}_2)$  and the band at  $920 \text{ cm}^{-1}$  to an overtone of  $\nu_{19}(\text{F}_2)$ . In the IR spectra at 90 K, one more band at  $938 \text{ cm}^{-1}$  is observed as a shoulder of the band at  $948 \text{ cm}^{-1}$ . The three bands at 938, 948 and  $958 \text{ cm}^{-1}$  cannot be assigned as the components of  $\nu_{18}(\text{F}_2)$  since  $\text{TMACl-d}_0$  has space group  $D_{4h}^7$  ( $z = 2$ ) at room temperature and according to group theoretical analysis the modes of species  $\text{F}_2$  can have only two  $A_{2u} + E_u$  IR active components. The band at  $938 \text{ cm}^{-1}$  could be arising due to phase transition but the same splitting is also observed in the cases of  $\text{TMABr-d}_0$  and  $\text{TMAI-d}_0$  which do not show any phase transitions in this temperature range. An alternative assignment, which looks more logical, is that the bands at 920 and  $938 \text{ cm}^{-1}$  are the components of overtone of  $\nu_{19}(\text{F}_2)$ . According to group theoretical analysis a mode of species  $\text{F}_2$  splits into  $A_{2u} + E_u$  IR active components whereas an overtone of modes of species  $\text{F}_2$  may split into

$A_{2u} + 2E_g$  IR active components under the space group  $D_{4h}^7$  through the site symmetry  $D_{2d}$  as shown in Table 3.4. Thus a number of components of overtone of  $\nu_{19}(F_2)$  may resonate with the components of  $\nu_{18}(F_2)$ .

### 3.6 RAMAN SPECTRA OF TMACl-d<sub>12</sub> IN PHASES III AND II

The relevant portions of the observed Raman spectra of TMACl-d<sub>12</sub> in phase III (at 300 K) and in phase II (at 448 and 300 K - on cooling under vacuum) are depicted in Fig. 3.7. The Raman spectrum at 90 K are also shown in the Fig. 3.7; but it is similar to the spectrum in phase III. The observed band positions with peak intensities, half-widths and relative integrated intensities and their assignments are given in Table 3.7.

The modes of C<sub>4</sub>N in TMACl-d<sub>12</sub> in both the phases have been assigned by correlating the Raman spectra of TMACl-d<sub>12</sub> in aqueous solution [8], Raman spectra of TMACl-d<sub>0</sub> in the two phases [2] and isotopic shift calculations [8]. Two bands at 808 and 813 cm<sup>-1</sup> are observed in phase III which shift to 809 and 816 cm<sup>-1</sup> in phase II. When the sample in phase II is cooled to room temperature the band at 809 cm<sup>-1</sup> further splits into two components at 806 and 810 cm<sup>-1</sup>. These split bands cannot be attributed to the C<sub>4</sub>N asymmetric stretch,  $\nu_{18}(F_2)$  as group theoretically the mode of F<sub>2</sub> species under point group symmetry T<sub>d</sub> may split into only two Raman active components of species A<sub>1</sub>+E under the space group, C<sub>3v</sub><sup>5</sup> through

the site symmetry  $C_{3v}$  in phase II [2]. Thus the triplet may be due to either structural change, distortion in symmetry of TM<sub>A</sub> ion or appearance of some overtone/combination of the lower frequency bands. Another alternative assignment is that the band at  $813\text{ cm}^{-1}$  in phase III is a component of  $CD_3$  rocking,  $\nu_{11}(F_1)$ . The isotopic shift ratio  $(\nu^D/\nu^H)$  for this band then turns out to be 0.761 which is quite close to the theoretically calculated value (0.774) [17]. The reason for the appearance of so strong a component of  $\nu_{11}(F_1)$  at  $813\text{ cm}^{-1}$  is that each of the modes  $\nu_{11}(F_1)$  and  $\nu_{18}(F_2)$  has at least one component of the same species in both the phases as shown in Table 3.9 and both  $\nu_{11}(F_1)$  and  $\nu_{18}(F_2)$  in  $TMACl-d_{12}$  fall very close. Therefore the  $CD_3$  rocking mode,  $\nu_{11}(F_1)$  gets intensity from  $C_4N$  asymmetric stretch,  $\nu_{18}(F_2)$  due to resonance interaction.

The bands in the region  $1040-1100\text{ cm}^{-1}$  in  $TMACl-d_{12}$  show temperature dependent behaviour similar to that of  $\nu_6(E)$  and  $\nu_{15}(F_2)$  in  $TMACl-d_0$ . Therefore the band at  $1052\text{ cm}^{-1}$  is assigned to  $\nu_6(E)$  and the bands at  $1066$  and  $1076\text{ cm}^{-1}$  are assigned to  $\nu_{15}(F_2)$  in the room temperature phase III. This assignment is in accordance with Berg's assignment in the Raman spectra of  $TMACl-d_{12}$  in aqueous solution [17].

The band at  $1191\text{ cm}^{-1}$  in polycrystalline  $TMACl-d_{12}$  can be assigned to either  $\nu_{16}(F_2)$  or  $\nu_{17}(F_2)$ . Kabisch et al. [19] have shown that the  $CD_3$  symmetric deformation,  $\nu_{16}(F_2)$  has very small intensity in the Raman spectra of deuterated ( $d_{12}$ ) tetramethyl ammonium iodide. In the Raman spectra of  $TMACl-d_{12}$

in aqueous solution a band at  $1192 \text{ cm}^{-1}$  is assigned as  $\text{CD}_3$  rocking mode,  $\nu_{17}(\text{F}_2)$  with the help of Teller Redlich product rule [17]. This gives an isotopic shift ( $\nu^{\text{D}}/\nu^{\text{H}}$ ) of 0.922 for  $\nu_{17}(\text{F}_2)$  whereas the calculated isotopic shift for this mode is 0.744. So the interpretation of band at  $1191 \text{ cm}^{-1}$  as  $\nu_{17}(\text{F}_2)$  in  $\text{TMACl-d}_{12}$  still needs a theoretical verification.

Methyl symmetric stretch,  $\nu_1(\text{A}_1)$  is quite difficult to assign due to appearance of a number of intense polarized bands in this region. Kabisch et al. [24] have calculated the value of unperturbed methyl symmetric stretch,  $\nu_1(\text{A}_1)$  as  $2947.5 \text{ cm}^{-1}$  for  $\text{TMACl-d}_0$  and  $2142 \text{ cm}^{-1}$  for  $\text{TMACl-d}_{12}$  in the Raman spectra of aqueous solutions, but the calculation of unperturbed  $\nu_1(\text{A}_1)$  contributed nothing significant to the assignment. The sharp band at  $2077 \text{ cm}^{-1}$  in the Raman spectrum of  $\text{TMACl-d}_{12}$  in phase III is tentatively assigned to  $\nu_1(\text{A}_1)$  since it does not show any splitting even at liquid nitrogen temperature as expected from group theoretical consideration [2].

The bands at  $2255$  and  $2273 \text{ cm}^{-1}$  are assigned to methyl asymmetric stretches,  $\nu_5(\text{E})$  and  $\nu_{13}(\text{F}_2)$ , respectively. Other bands in the methyl stretching region are also assigned tentatively as overtones/combination of lower frequency bands as given in Table 3.7.

### 3.7 PHASE TRANSITIONS

Tetramethyl ammonium chloride (TMACl-d<sub>6</sub>) undergoes four successive phase transitions detected by differential thermal analysis [8, 9, 25, 26], nuclear magnetic resonance [10], proton spin-lattice relaxation [27] and electron paramagnetic resonance [11] studies. The details of phases and transitions are compiled in Table 3.10.

The phase transition temperatures are determined with the temperature dependence of  $\nu_6(E)$  and  $\nu_{15}(F_2)$  modes for transitions III  $\rightarrow$  II  $\rightarrow$  I as shown in Figs. 3.8 (without vacuum) and 3.9 (under continuous vacuum). The transition III  $\rightarrow$  IV is followed by monitoring the temperature dependence of  $\nu_{16}(F_2)$  as shown in Fig. 3.10. It is observed from Fig. 3.8 that in transition III  $\rightarrow$  II the bands at 1454, 1477 and 1483  $\text{cm}^{-1}$  start to diminish at 412 K and a new band starts to appear at 1462  $\text{cm}^{-1}$ , the latter band gaining intensity with increase in temperature. At  $\sim$ 430 K the bands at 1454, 1477 and 1483  $\text{cm}^{-1}$  completely disappear and the band at 1462  $\text{cm}^{-1}$  shifts to 1466  $\text{cm}^{-1}$  and becomes fairly strong. So it is seen here that the phase transition III  $\rightarrow$  II is a second order transition taking place over a temperature range of 18 K. Pistorius and Gibson [8] have suggested that III  $\rightarrow$  II transition has a thermal hysteresis of 18-24 K. We have observed that the transition temperature depends on the initial moisture content and the rate of heating. On very slow heating it is found to be  $\sim$ 20 K higher than the

reported one. But in the presence of much moisture and fast heating it is found to occur around 390 K. We have further observed that the phase transition III  $\rightarrow$  II in TMACl-d<sub>6</sub> occurs at 367  $\pm$  2 K on keeping the sample under continuous vacuum during the investigation (Fig. 3.9). The variations of peak intensities of  $\nu_5(E)$  ( $1454\text{ cm}^{-1}$ ) and  $\nu_{15}(F_2)$  ( $1477$  and  $1483\text{ cm}^{-1}$ ) with temperature are shown in Fig. 3.11. On cooling the sample under vacuum to room temperature from 400 K the band at  $1466\text{ cm}^{-1}$  gains in intensity and shifts to  $1468\text{ cm}^{-1}$ . Thus the phase transition III  $\rightarrow$  II is irreversible and phase II is metastable below 367 K. As soon as we release the water vapour to the sample in phase II at room temperature, it transforms to phase III. The arrangement for transferring water vapour to the sample under vacuum is shown in Fig. 3.12. Thus phase III is stable only in presence of a small amount of moisture. Pistorius and Gibson [8] have shown that only 0.5% water is sufficient for the stability of phase III.

In the transition II  $\rightarrow$  I the band at  $1466\text{ cm}^{-1}$  disappears in an hour when the sample is kept at constant temperature at 540 K just above the reported transition temperature (Fig. 3.8). Other bands also disappear in phase I except for the bands of C<sub>4</sub>N skeleton which are found to be very weak.

On lowering the temperature in phase transition III  $\rightarrow$  IV the band at  $1402\text{ cm}^{-1}$  having slight asymmetry on the lower frequency side at  $1398\text{ cm}^{-1}$ , first suddenly splits into two components near the transition temperature and finally into

three components at 1392, 1399 and 1407  $\text{cm}^{-1}$  within a temperature interval of  $\sim 10$  K (Fig. 3.10). The sudden splitting of band at 1402  $\text{cm}^{-1}$  into three components at 185 K indicates that the transition III  $\rightarrow$  IV is first order. On heating back we observed reversal of the same pattern, indicating that the transition III  $\rightarrow$  IV is reversible without hysteresis.

The temperature dependence of  $\text{CD}_3$  asymmetric deformation  $\nu_6(\text{E})$  and  $\nu_{15}(\text{F}_2)$  in the Raman spectra of  $\text{TMACl-d}_{12}$  is shown in Fig. 3.13. The variations of peak intensities of the components of  $\nu_{15}(\text{F}_2)$  (at 1066 and 1076  $\text{cm}^{-1}$ ) with temperature is shown in Fig. 3.14;  $\nu_6(\text{E})$  at 1052  $\text{cm}^{-1}$  is too weak to monitor its variation with temperature. A new band at 1058  $\text{cm}^{-1}$  appears at 407 K which gains intensity upto 430 K. A component of  $\nu_{15}(\text{F}_2)$  at 1076  $\text{cm}^{-1}$  completely disappears around 430 K. Thus the phase transition III  $\rightarrow$  II in  $\text{TMACl-d}_{12}$  starts at  $407 \pm 5$  K and completes around 430 K. The transition III  $\rightarrow$  II in  $\text{TMACl-d}_{12}$  is also found to be irreversible in the absence of moisture.

On cooling the sample to liquid nitrogen temperature we do not get any sudden changes in the spectra. So the phase transition III  $\rightarrow$  IV does not occur in  $\text{TMACl-d}_{12}$  in this temperature range.

### 3.8 CONCLUSION

For distinguishing the bands of different species in all the phases, single-crystal Raman spectra in different orientations are required. With the splitting of the bands of

species  $F_2$  in  $\text{TMA-d}_0$  ion under molecular symmetry  $T_d$  into three, the space group for phase IV is suggested to be  $D_4^1$  ( $z = 2$ ), it needs verification by X-ray data which still seek to be determined for this phase as well as phase V.

It is clear from the above studies that the traces of water present in  $\text{TMACl-d}_0$  and  $\text{TMACl-d}_{12}$  play a major role in  $\text{III} \rightarrow \text{II}$  phase transition. But the change in  $\text{III} \rightarrow \text{II}$  transition temperature on deuteration and the non-existence of lower temperature phase in  $\text{TMACl-d}_{12}$  similar to those in  $\text{TMACl-d}_0$  suggest that the traces of water are not the only responsible entities for phase transitions in the tetramethyl ammonium chlorides. Among the normal ( $d_0$ ) tetramethyl ammonium halides (i.e. chloride, bromide and iodide), which are isostructural [4-6], only  $\text{TMACl-d}_0$  undergoes four successive phase transitions. Pistorius and Gibson [8] have pointed out that the occurrence of phase transitions in  $\text{TMACl-d}_0$  only may be found in the generalized phase diagram of ammonium halides. The generalized phase diagram of ammonium halides [7] is shown in Fig. 3.15. Our observations would lead to conclude that  $\text{TMACl-d}_{12}$  lies in between  $\text{TMACl-d}_0$  and tetramethyl ammonium bromide in the generalized phase diagram of tetramethyl ammonium halides.

For phase I the earlier suggested space group  $O_h^5$  ( $z = 4$ ) is inherently inconsistent and has to be reinvestigated crystallographically.

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Table 3.1 : Values of various parameters used to determine the positions of various atoms in crystal structure (see Fig. 3.1) and unit cell dimensions for tetramethyl ammonium halides [4].

|                      | $(\text{CH}_3)_4\text{NCl}$ | $(\text{CH}_3)_4\text{NBr}$ | $(\text{CH}_3)_4\text{NI}$ |
|----------------------|-----------------------------|-----------------------------|----------------------------|
| P                    | 0.361                       | 0.375                       | 0.394                      |
| S                    | 0.339                       | 0.335                       | 0.347                      |
| r                    | 0.156                       | 0.153                       | 0.164                      |
| C-H bond length      | 1.62 Å                      | 1.63 Å                      | 1.64 Å                     |
| N-C bond length      | 1.46 Å                      | 1.45 Å                      | 1.51 Å                     |
| Unit cell parameters | $a$<br>$c$                  | 6.278 Å                     | 6.118 Å                    |
|                      |                             | 4.556 Å                     | 4.366 Å                    |

Table 3.2 : Classification of the modes of  $(\text{CH}_3)_4\text{N}^+$  ion under the point group  $T_d$  (same for both eclipsed and staggered configurations).

| $T_d$          | E | $8C_3$ | $3C_2$ | $6\sigma_d$ | $6S_4$ | $N_1$           | Activity |       |
|----------------|---|--------|--------|-------------|--------|-----------------|----------|-------|
|                |   |        |        |             |        |                 | IR       | Raman |
| $A_1$          | 1 | 1      | 1      | 1           | 1      | 3               | a        | ia    |
| $A_2$          | 1 | 1      | 1      | -1          | -1     | 1               | ia       | ia    |
| E              | 2 | -1     | 2      | 0           | 0      | 4               | a        | ia    |
| F <sub>1</sub> | 3 | 0      | -1     | -1          | 1      | $R_X, R_Y, R_Z$ | ia       | ia    |
| F <sub>2</sub> | 3 | 0      | -1     | 1           | -1     | $T_X, T_Y, T_Z$ | a        | a     |

|                  |    |     |     |    |    |  |  |
|------------------|----|-----|-----|----|----|--|--|
| $\varphi$        | 0  | 120 | 180 | 0  | 90 | $\varphi$                                      | - Angle of rotation.                                     |
| $\omega_R$       | 17 | 2   | 1   | 5  | 1  | $\omega_R$                                     | - Number of atoms remains invariant under the operation. |
| $X_{T(R)45}$     | 0  | 1   | 5   | -1 |    | $X_{T(R)}$                                     | - Character for internal vibrational modes.              |
| $X_{\alpha(R)6}$ | 0  | 2   | 2   | 0  |    | $X_T(R) = (\omega_R - 2) (1 + 2 \cos \varphi)$ | for proper rotations                                     |
| $X_{M(R)3}$      | 0  | -1  | 1   | -1 |    | $= \omega_R (-1 + 2 \cos \varphi)$             | for improper rotations                                   |

$\varphi$  - Angle of rotation.

$\omega_R$  - Number of atoms remains invariant under the operation.

$X_{T(R)}$  - Character for internal vibrational modes.

$X_T(R) = (\omega_R - 2) (1 + 2 \cos \varphi)$  for proper rotations

$= \omega_R (-1 + 2 \cos \varphi)$  for improper rotations

$X_{\alpha(R)}$  - Character for polarizability tensor.

$X_{\alpha(R)} = 2 + 2 \cos \varphi + 2 \cos(2\varphi)$  + for proper rotations

- for improper rotations

$X_M(R)$  - Character for dipole moment  
 $X_M(R) = +1 + 2 \cos \varphi$  - for proper rotations  
 $X_M(R) = -1$  - for improper rotations.

Number of fundamental of species  $i$   $N_i = \frac{1}{N_G} \sum n_e X_T(R) X_i(R)$

The modes of species  $i$  are Raman active  $N_i^R = \frac{1}{N_G} \sum n_e X_\alpha(R) X_i(R) \neq 0$

The modes of species  $i$  are IR active  $N_i^{IR} = \frac{1}{N_G} \sum n_e X_M(R) X_i(R) \neq 0$

$N_G$  - Number of elements of the group ( $= 24$ )  
 $n_e$  - Number of elements in each class (e.g. for E,  $n_E = 1$ )  
 $X_i(R)$  - Character of species  $i$  in each class.

$$N_{A_1} = \frac{1}{24} [1x45x1 + 8x0x1 + 3x1x1 + 6x5x1 + 6x-1x1] = 3$$

$$N_{A_1}^R = \frac{1}{24} [1x6x1 + 8x0x1 + 3x2x1 + 6x2x1 + 6x0x1] = 1$$

$$N_{A_1}^{IR} = \frac{1}{24} [1x3x1 + 8x0x1 + 3x-1x1 + 6x1x1 + 6x-1x1] = 0$$

$X_\alpha$  - active,  $X_\alpha$  - inactive.

For the analysis in detail, see refs. [4, 5, 18].

Table 3.3 : Nomenclature of the normal modes of  $(\text{CH}_3)_4\text{N}^+$  ion under the point group symmetry  $\text{T}_d$  [14].

| Description                    | Symmetry class of point group $\text{T}_d$ |                          |             |                             |              |                             |
|--------------------------------|--|--------------------------|-------------|-----------------------------|--------------|-----------------------------|
|                                | $\text{A}_1$                               | $\text{A}_2$             | $\text{E}$  | $\text{F}_1$                | $\text{F}_2$ |                             |
| $\text{CH}_3$ asy. str.        | •••••                                      |                          | $\nu_5$ (E) | $\nu_9$ ( $\text{F}_1$ )    |              | $\nu_{13}$ ( $\text{F}_2$ ) |
| $\text{CH}_3$ asy. str.        |  | $\nu_1$ ( $\text{A}_1$ ) | •••••       | •••••                       |              | $\nu_{14}$ ( $\text{F}_2$ ) |
| $\text{CH}_3$ asy. def.        | •••••                                      |                          | $\nu_6$ (E) | $\nu_{10}$ ( $\text{F}_1$ ) |              | $\nu_{15}$ ( $\text{F}_2$ ) |
| $\text{CH}_3$ sym. def.        |  | $\nu_2$ ( $\text{A}_1$ ) | •••••       | •••••                       |              | $\nu_{16}$ ( $\text{F}_2$ ) |
| $\text{CH}_3$ rock.            | •••••                                      |                          | $\nu_7$ (E) | $\nu_{11}$ ( $\text{F}_1$ ) |              | $\nu_{17}$ ( $\text{F}_2$ ) |
| $\text{C}_4\text{N}$ asy. str. | •••••                                      |                          |             | •••••                       |              | $\nu_{18}$ ( $\text{F}_2$ ) |
| $\text{C}_4\text{N}$ sym. str. |  | $\nu_3$ ( $\text{A}_1$ ) | •••••       | •••••                       |              | •••••                       |
| $\text{C}_4\text{N}$ asy. def. | •••••                                      |                          | •••••       | •••••                       |              | •••••                       |
| $\text{C}_4\text{N}$ sym. def. | •••••                                      |                          | $\nu_8$ (E) | •••••                       |              | $\nu_{19}$ ( $\text{F}_2$ ) |
| $\text{CH}_3$ torsion          | •••••                                      | $\nu_4$ ( $\text{A}_2$ ) | •••••       | $\nu_{12}$ ( $\text{F}_1$ ) | •••••        |                             |
| Activity*                      | R pol                                      | i <sub>a</sub>           | R dep       | i <sub>a</sub>              | R dep, IR    |                             |

\* R - Raman, pol - polarized, dep - depolarized, IR - infrared, i<sub>a</sub> - inactive.

Table 3.4 : Correlation between the species of molecular point group and factor groups through the species of site symmetries for TMA ion in phases II and III.

| Phase II     |               | Phase III          |               |
|--------------|---------------|--------------------|---------------|
| Factor group | Site symmetry | Molecular symmetry | Site symmetry |
| $C_{3v}$     | $C_{3v}$      | $T_d$              | $D_{2d}$      |
|              |               |                    | $D_{4h}$      |

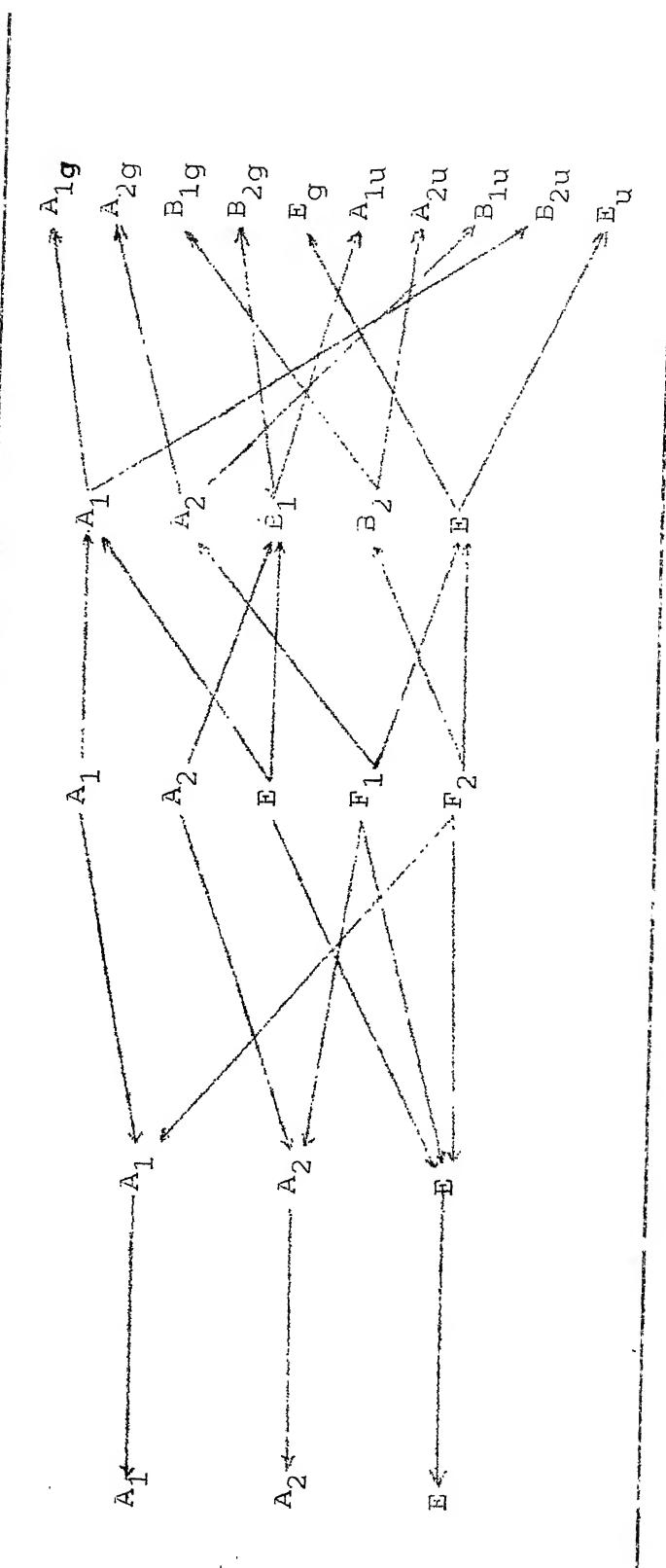


Table 3.5 : Band-positions (in  $\text{cm}^{-1}$ ) of the observed bands in the Raman and IR spectra of normal ( $\text{d}_0$ ) and perdeuterated ( $\text{d}_{12}$ ) tetramethyl ammonium chloride in aqueous solutions and their assignments.

| TMACl- $\text{d}_0$         |       | TMACl- $\text{d}_{12}$           |              | Assignments   |
|-----------------------------|-------|----------------------------------|--------------|---|
|                             | Raman | IR                               | IR           |   |
| Diluted solution<br>(0.5 M) |       | Concentrated solution<br>(6.0 M) |              |   |
| 1                           | 2     | 3                                | 4            | 9   |
| 370(18, 7)dp                |       | 370(16, 7)                       |              | $\nu_8$ (E)   |
| 457(22, 7)dp                |       | 457(16, 9)                       |              | $\nu_{19}$ ( $\text{F}_2$ )                               |
| 736(15, 16)p                |       | 735(20, 14)                      |              | $2\nu_8$ (E)  |
| 755(9, 38)p                 |       | 754(9, 54)                       |              | $\nu_1$ ( $\text{A}_1$ )                                  |
|                             |       |                                  | 679          |   |
|                             |       |                                  | 920 m        | $2\nu_{15}$ ( $\text{F}_2$ )                              |
|                             |       |                                  | 950vs        | $\nu_{18}$ ( $\text{F}_2$ )                               |
|                             |       |                                  | 922          | $\nu_7$ (E)   |
|                             |       |                                  | 1290m 1192   | $\nu_{17}$ ( $\text{F}_2$ )                               |
|                             |       |                                  | 1415s        | $\nu_{16}$ ( $\text{F}_2$ )                               |
|                             |       |                                  | 1144p        | $\nu_2$ ( $\text{A}_1$ )                                  |
|                             |       |                                  | 1485s 1057dp | $\nu_6$ (E)   |
|                             |       |                                  | 1062         | $\nu_{15}$ ( $\text{F}_2$ )                               |
|                             |       |                                  | 2364         | .....   |
|                             |       |                                  | 2490         | $\nu_{11}$ ( $\text{E}_1$ ) + $\nu_{16}$ ( $\text{F}_2$ ) |

Table 3.5 contd.....

|              |               |               |      |                                      |
|--------------|---------------|---------------|------|--------------------------------------|
| 2520         | ••••          | ••••          | •••• | $\nu_{11(F_1)+\nu_{15(F_2)}}$        |
| 2590         | ••••          | ••••          | •••• | •••••                                |
| 2618         | ••••          | ••••          | •••• | •••••                                |
| 2660         | ••••          | ••••          | •••• | •••••                                |
| 2770         | ••••          | ••••          | •••• | $\nu_{15(F_2)+\nu_{17(F_2)}}$        |
| 2848(25)     | 2824          | 2107          | •••• | $2\nu_{16(F_2)}$                     |
| 2880(-2)     | 2880(23,8)    | 2880(23,8)    | •••• | $\nu_{16(F_2)+\nu_6(E)}$             |
| 2912(6)      | 2906(20,6)    | 2906(20,6)    | •••• | $2\nu_6(E)$                          |
| 2941(12)     | 2939(12)      | 2939(12)      | •••• | $\nu_6(E)+\nu_{15(F_2)}$             |
| 2970(7)      | 2963(24,123)  | 2963(24,123)  | •••• | $2\nu_{15(F_2)}$                     |
| 2987(16,100) | 2991(16,100)  | 2991(16,100)  | •••• | $\nu_1(A_1)$                         |
| 3033(25,125) | 3043(20,50)dp | 3043(20,50)dp | •••• | $\nu_5(E) \text{ or } \nu_{15(F_2)}$ |
| 3980         | ••••          | ••••          | •••• | $\nu_{13(F_2)+\nu_{18(F_2)}}$        |

columns 2, 3, 5 and 7 indicate the observed wavenumbers  $\text{cm}^{-1}$ . The figures in parentheses are each wavenumber in columns 1 and 3 denote the half-width and the relative integrated intensities respectively.

Columns 2 and 4 indicate the calculated values ( $\text{cm}^{-1}$ ) of overtone/combination band in  $\text{CH}_3$  stretching region as shown in column 8. The figures in parentheses in these columns represent the differences of the harmonic values (as expected from the assignments in column 8) and the actual observed wavenumbers shown in columns 1 and 3.

Columns 8 and 9 represent the assignments based on Fermi-resonance and anharmonicity and dynamical distortion of the  $C_4N$  - skeleton , respectively.

† The assignment of the bands not given in this column is identical to that of column 8.

\* Raman and IR data for TMAC1-d<sub>12</sub> are taken from ref. [17].

V - very, s - strong, m - medium and w - weak.

Selection rules for overtones and combinations are

$$F_2 \times F_2 = A_1 + E + F_1 + F_2, \quad E \times E = A_1 + A_2 + E, \quad E \times F_2 = F_1 + F_2$$

Table 3.6 : Correlation of the  $\text{CH}_3$  stretching vibrations having point group  $C_{3v}$  with corresponding vibrations in TMA symmetries  $T_d$  or  $C_{3v}$ .

| $\text{CH}_3$ stretching vibrations                                    |  |  |
|--|--|--|
| Isolated $\text{CH}_3$   | $\text{CH}_3$ in TMA units             |  |
| $C_{3v}$   | $T_d$                                  | $C_{3v}$   |
| Totally symmetric<br>$\text{CH}_3$ stretching<br>vibration, $A_1(R)$   | $A_1(R)$<br>$F_2(R, \text{IR})$        | $A_1(R(p), \text{IR})$<br>$A_1(R(p), \text{IR})$<br>$E(R(dp), \text{IR})$                                  |
| Asymmetric $\text{CH}_3$<br>stretching vibration,<br>$E(R, \text{IR})$ | $E(R)$<br>$F_1$<br>$F_2(R, \text{IR})$ | $E(R(dp), \text{IR})$<br>$E(R(dp), \text{IR})$<br>$A_2$<br>$E(R(dp), \text{IR})$<br>$A_1(R(p), \text{IR})$ |

The notations regarding species are discussed in the text. The activities in Raman (R) and infrared (IR) are given for ready reference.

p - polarized, dp - depolarized.

Table 3.7: Band-positions ( $\text{cm}^{-1}$ ) with half-additions and relative integrated intensities in different phases of normal ( $\text{I}_0$ ) and pentamerized ( $\text{I}_{1/2}$ ) tetramethyl ammonium chlorides (kept under continuous vacuum).

|            |              | TNC1-d <sub>0</sub> |              |              |             |             |             | TNC1-d <sub>1/2</sub> |             |             |             |             |                      |
|------------|--------------|---------------------|--------------|--------------|-------------|-------------|-------------|-----------------------|-------------|-------------|-------------|-------------|----------------------|
|            |              | Raman               |              |              | IR          |             |             | Raman                 |             |             | IR          |             |                      |
| Phase I    |              | Phase II            |              | Phase III    |             | Phase IV    |             | Phase II              |             | Phase III   |             | Phase IV    |                      |
| 600 K      | 390 K        | 300 K               | 300 K        | 90 K         | 90 K        | 440 K       | 300 K       | 300 K                 | 300 K       | 300 K       | 300 K       | 300 K       | 300 K                |
| 1          | 2            | 3                   | 4            | 5            | 6           | 7           | 8           | 9                     | 10          | 11          | 12          | 13          |                      |
| 368 (12,3) | 370 (8,2)    | 376 (5,1)           | 376 (5,1)    | 355w         | 375w        | 316 (15,6)  | 314 (16,5)  | 319 (9,4)             | 319 (9,4)   | 332 (6,3)   | 332 (6,3)   | 332 (6,3)   | $\nu_3 (\text{E})$   |
| 388        | 388          | 388 (6,4)           | 389 (4,4)    | 389          | 389         | 389         | 389         | 389                   | 389         | 389         | 389         | 389         | $\nu_3 (\text{E})$   |
| 454        | 454 (8,11)   | 456 (8,10)          | 456 (8,10)   | 456w         | 456w        | 386 (9,34)  | 386 (9,34)  | 387 (6,10)            | 387 (6,10)  | 392 (5,10)  | 392 (5,10)  | 392 (5,10)  | $\nu_1 (\text{F}_2)$ |
| 459        | 459 (7,25)   | 459 (6,22)          | 459 (6,8)    | 464 (5,6)    | 464 (5,6)   | 464 (5,6)   | 464 (5,6)   | 464 (5,6)             | 464 (5,6)   | 464 (5,12)  | 464 (5,12)  | 464 (5,12)  | $\nu_1 (\text{F}_2)$ |
| 733        | 733 (16,16)  | 734 (14,9)          | 730 (30,2)   | 736 (16,2)   | 736 (16,2)  | 736 (16,2)  | 736 (16,2)  | 736 (16,2)            | 736 (16,2)  | 736 (16,2)  | 736 (16,2)  | 736 (16,2)  | $\nu_3 (\text{A}_1)$ |
| 754        | 754 (6,39)   | 754 (5,39)          | 760 (10,39)  | 758 (10,29)  | 758 (10,29) | 758 (10,29) | 758 (10,29) | 758 (10,29)           | 758 (10,29) | 758 (5,35)  | 758 (5,35)  | 758 (5,35)  | $\nu_3 (\text{A}_1)$ |
| 918        | 918 (20,6)   | 917 (20,5)          | 930 (18,2)   | 987 (17,2)   | 920w        | 920w        | 920w        | 920w                  | 920w        | 920w        | 920w        | 920w        | $\nu_1 (\text{F}_2)$ |
| 944        | 944 (6,14)   | 944 (6,14)          | 945 (3,1)    | 945 (3,1)    | 945         | 945         | 945         | 945                   | 945         | 945         | 945         | 945         | $\nu_1 (\text{F}_2)$ |
| 945        | 945 (5,12)   | 940 (7,20)          | 946 (5,5,30) | 946 (5,5,30) | 946w        | 946w        | 946w        | 946w                  | 946w        | 946w        | 946w        | 946w        | $\nu_1 (\text{F}_2)$ |
| 1068       | 1068 (8,2)   | 1063 (6,2)          | 1063 (6,2)   | 1063w        | 1063w       | 953w        | 953w        | 953w                  | 953w        | 953w        | 953w        | 953w        | $\nu_1 (\text{F}_2)$ |
| 1100       | 1100 (4,6)   | 1103 (4,3)          | 1103 (4,3)   | 1103 (4,3)   | 1103 (4,3)  | 1103 (4,3)  | 1103 (4,3)  | 1103 (4,3)            | 1103 (4,3)  | 1103 (4,3)  | 1103 (4,3)  | 1103 (4,3)  | $\nu_1 (\text{F}_1)$ |
| 1192       | 1192 (10,1)  | 1197 (6,1)          | 1197 (6,1)   | 1197 (6,1)   | 1197 (6,1)  | 1197 (6,1)  | 1197 (6,1)  | 1197 (6,1)            | 1197 (6,1)  | 1197 (6,1)  | 1197 (6,1)  | 1197 (6,1)  | $\nu_1 (\text{F}_1)$ |
| 1282       | 1282 (11,3)  | 1286 (5,9)          | 1291 (5,10)  | 1291 (5,10)  | 1291 (5,10) | 1291 (5,10) | 1291 (5,10) | 1291 (5,10)           | 1291 (5,10) | 1291 (5,10) | 1291 (5,10) | 1291 (5,10) | $\nu_1 (\text{F}_1)$ |
| 1293       | 1293 (16,9)  | 1295 (5,9)          | 1295 (5,9)   | 1295w        | 1295w       | 1295w       | 1295w       | 1295w                 | 1295w       | 1295w       | 1295w       | 1295w       | $\nu_1 (\text{F}_1)$ |
| 1398       | 1398 (8,5)   | 1392 (4,3)          | 1392 (4,3)   | 1392 (4,3)   | 1392 (4,3)  | 1392 (4,3)  | 1392 (4,3)  | 1392 (4,3)            | 1392 (4,3)  | 1392 (4,3)  | 1392 (4,3)  | 1392 (4,3)  | $\nu_1 (\text{F}_1)$ |
| 1482       | 1482 (6,8)   | 1397 (4,4)          | 1397 (4,4)   | 1397 (4,4)   | 1397 (4,4)  | 1397 (4,4)  | 1397 (4,4)  | 1397 (4,4)            | 1397 (4,4)  | 1397 (4,4)  | 1397 (4,4)  | 1397 (4,4)  | $\nu_1 (\text{F}_1)$ |
| 1493       | 1493 (14,25) | 1485 (7,15)         | 1487 (5,3)   | 1487 (5,3)   | 1487 (5,3)  | 1487 (5,3)  | 1487 (5,3)  | 1487 (5,3)            | 1487 (5,3)  | 1487 (5,3)  | 1487 (5,3)  | 1487 (5,3)  | $\nu_1 (\text{F}_1)$ |
|            | ...          | ...                 | ...          | ...          | ...         | ...         | ...         | ...                   | ...         | ...         | ...         | ...         |                      |
|            |              |                     |              |              |             |             |             |                       |             |             |             |             |                      |
|            |              |                     |              |              |             |             |             |                       |             |             |             |             |                      |

The data on  $\text{FeCl}_3\text{-I}_2$  are taken from ref. [17]. The figures in the parentheses with each wavenumber denote the half-widths ( $\text{cm}^{-1}$ ) and relative integrated intensities, respectively.

Table 3.8 : The numbers and types of vibrations related to  $\text{CH}_3$  stretching (or deformation) modes in phases II and III and TMA ions.

| Isolated $\text{CH}_3$<br>( $\text{C}_{3v}$ ) CH<br>vibrations<br>(stretch or<br>deformation) | TMA ( $T_d$ ) |                           | Phase II ( $Z=1$ ) |                       | Phase III ( $Z = 2$ )  |  |
|---|---------------|---------------------------|--------------------|-----------------------|--|--|
|   | Species       | Notations for<br>CH modes | $\text{C}_{3v}$    |                       | $\text{D}_{4h}$  |  |
|   |               | Str.                      | Def.               |                       |  |  |
| $A_1$   | $A_1^*$       | $\nu_1$                   | $\nu_2$            | $A_1^*$               | $A_{1g}^* + B_{2u}$  |  |
| Sym.  | $F_2^*$       | $\nu_{14}$                | $\nu_{16}$         | $A_1^* + E^*$         | $B_{1g}^* + E_g^* + A_{2u} + E_u$  |  |
| $E$   | $E^*$         | $\nu_5$                   | $\nu_6$            | $E^*$                 | $A_{1g}^* + B_{2g}^* + A_{1u} + B_{2u}$  |  |
| $E$   |               |                           |                    |                       |  |  |
| Asym.   | $F_1$         | $\nu_9$                   | $\nu_{10}$         | $A_2 + E^*$           | $A_{2g} + E_g^* + B_{1u} + E_u$  |  |
|   | $F_2^*$       | $\nu_{18}$                | $\nu_{15}$         | $A_1 + E^*$           | $B_{1g}^* + E_g^* + A_{2u} + E_u$  |  |
| Total number of<br>bands expected   |               |                           |                    | $3A_1^* + A_2 + 4E^*$ | $2A_{1g}^* + 2A_{2g} + 2B_{1g}^* + B_{2g}^* +$<br>$3E_g^* + A_{1u} + 2A_{2u} + B_{1u} +$<br>$2B_{2u} + 3E_u$ |  |

\* Denotes a Raman active species.

Table 3.9 : The factor group splittings of the modes of species  $F_1$  and  $F_2$  under the point group symmetry  $T_d$  for the TMA ion in phase III [ $D_{4h}^7$  ( $z = 2$ )] through the site  $D_{2d}$  and in phase II [ $C_{3v}^5$  ( $z = 1$ )] through the site  $C_{3v}$ .

| Species | Phase III ( $z = 2$ )                 | Phase II ( $z = 1$ ) |
|---------|---------------------------------------|----------------------|
|         | $D_{4h}$                              | $C_{3v}$             |
| $F_1$   | $A_{2g} + E_g^*$ + $B_{1u}$ + $E_u$   | $A_2 + E^*$          |
| $F_2$   | $B_{1g}^* + E_g^*$ + $A_{2u}$ + $E_u$ | $A_1^* + E^*$        |

\* Denotes a Raman active species.

Table 3.10 : The known phases and transition temperatures for normal ( $d_0$ ) tetramethyl ammonium chloride.

| Phase | Transition temperature | Type and nature       | Space Group            | Structure    |
|-------|------------------------|-----------------------|------------------------|--------------|
| I     | 536 K                  | Reversible            | $O_h^5$ ( $z = 4$ )    | fcc          |
| II    | 413 K*                 | Irreversible          | $C_{3v}^5$ ( $z = 1$ ) | Rhombohedral |
| III   | 1849 K                 | $\lambda$ -transition | $D_{4h}^7$ ( $z = 2$ ) | Tetragonal   |
| IV    | 75.8 K                 | First order           | ?                      | Tetragonal   |
| V     |                        |                       | ?                      | ?            |

\* Presently observed at  $368 \pm 2$  K when the sample is kept in the cell under continuous evacuation.

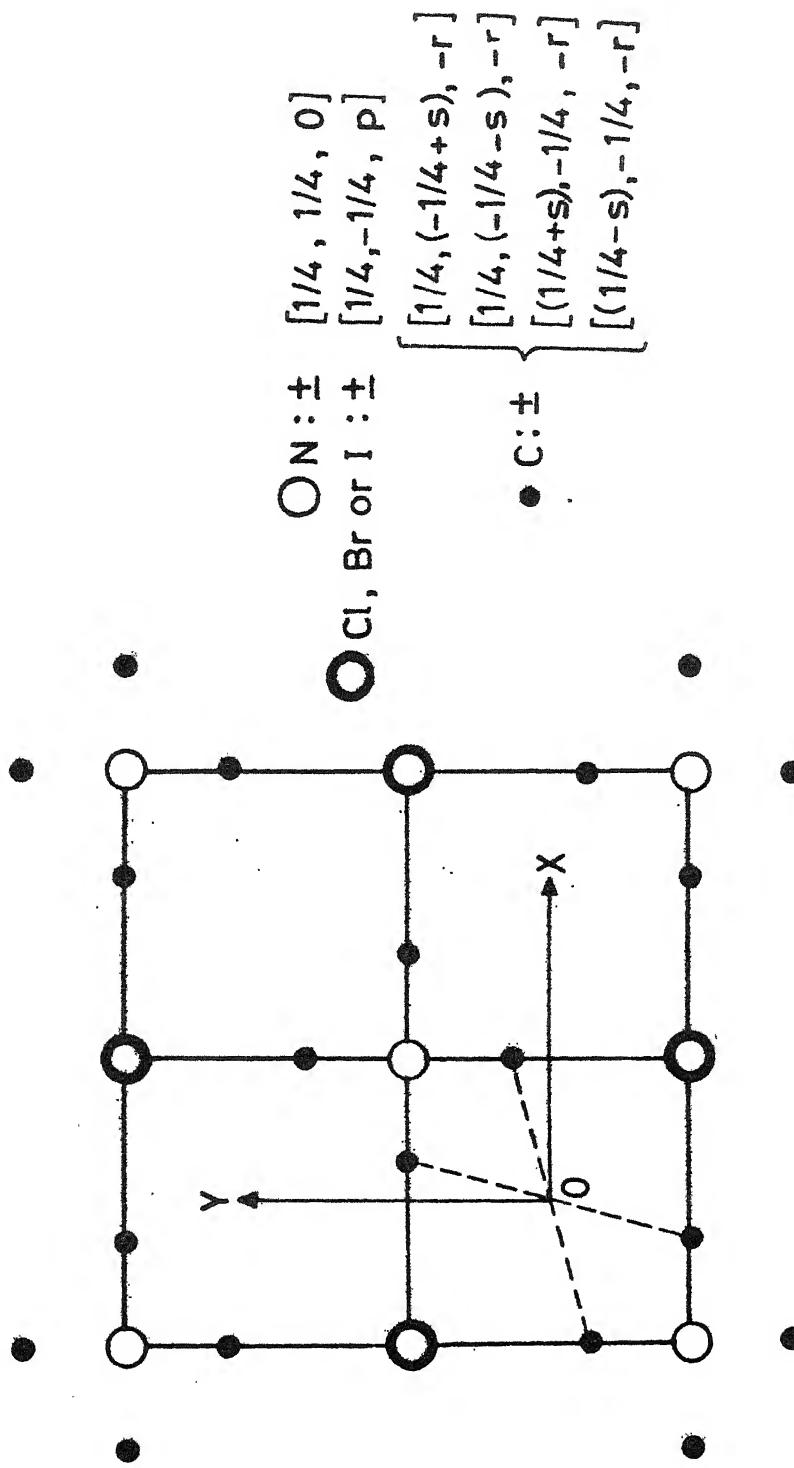


Fig. 3.1 Crystal structure of tetramethyl ammonium halides: projection in XY-plane (after Veggard and Sollesnes [4]). Various parameters used to determine the positions of atoms are given in Table 3.1.

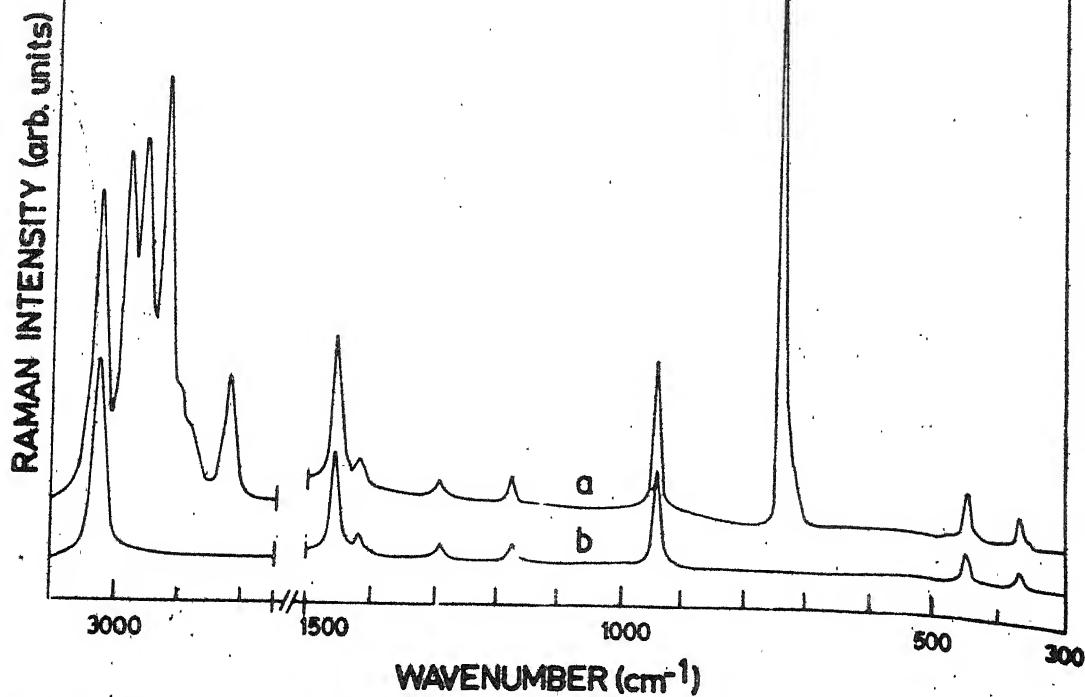


Fig. 3.2 Raman spectra of TMACl- $d_6$  in aqueous solution of 6.0 M:  
(a) Parallel and (b) Perpendicular polarizations.

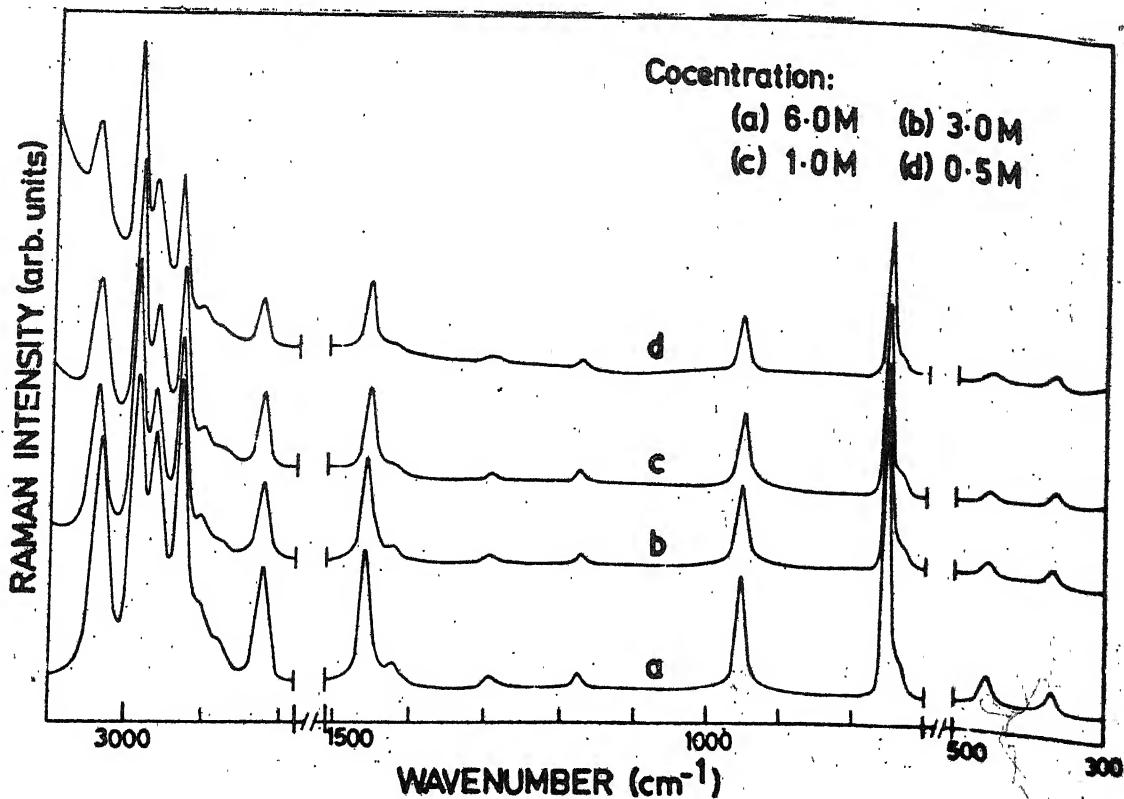


Fig. 3.3 Raman spectra of TMACl- $d_6$  in aqueous solutions with varying concentrations.

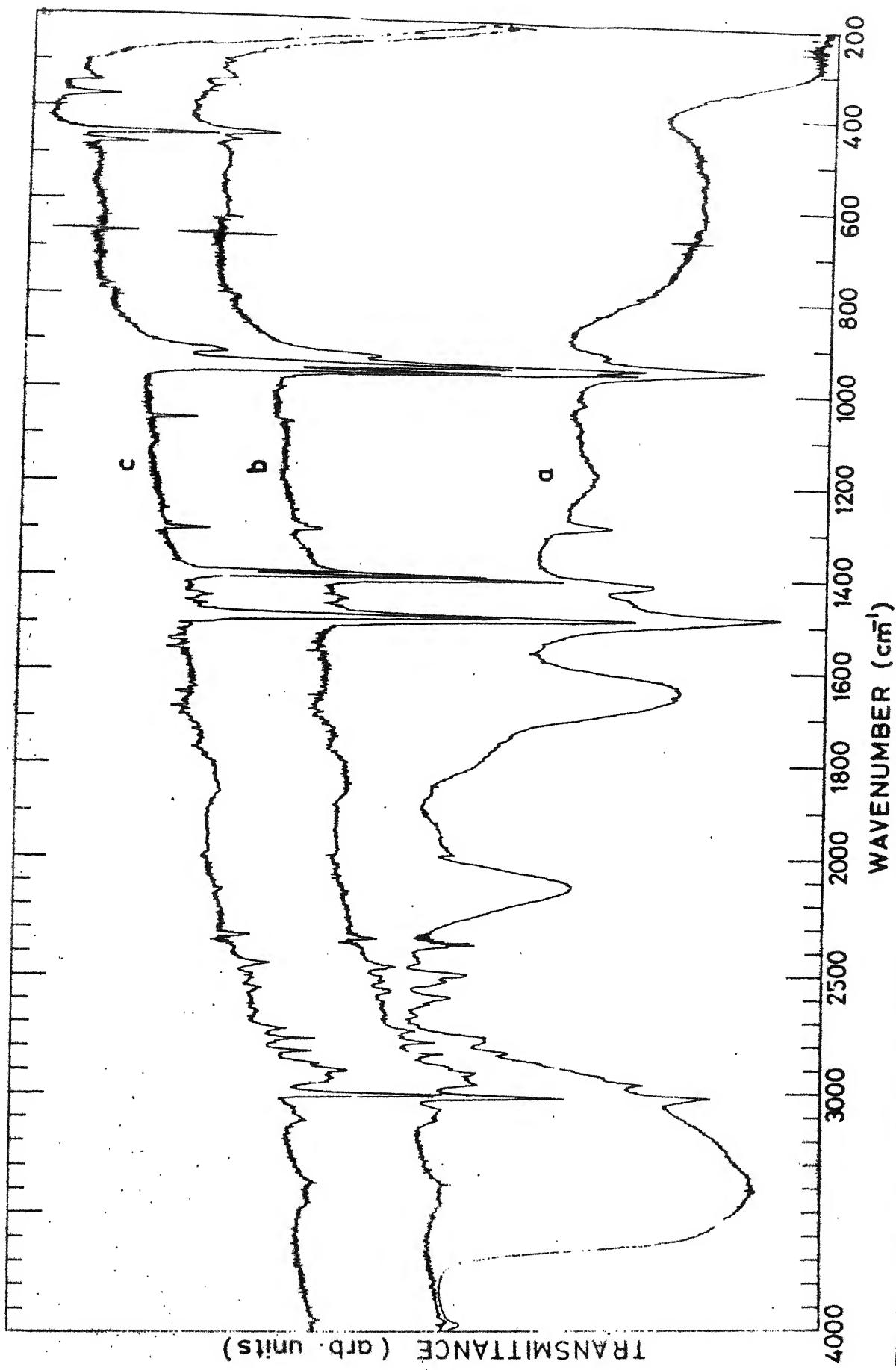


Fig. 3.4 Infrared spectra of TMACl-d<sub>6</sub>, (a) in aqueous solution kept between AgCl windows, (b) in KBr pellet at 300 K and (c) in KBr pellet at 90 K.

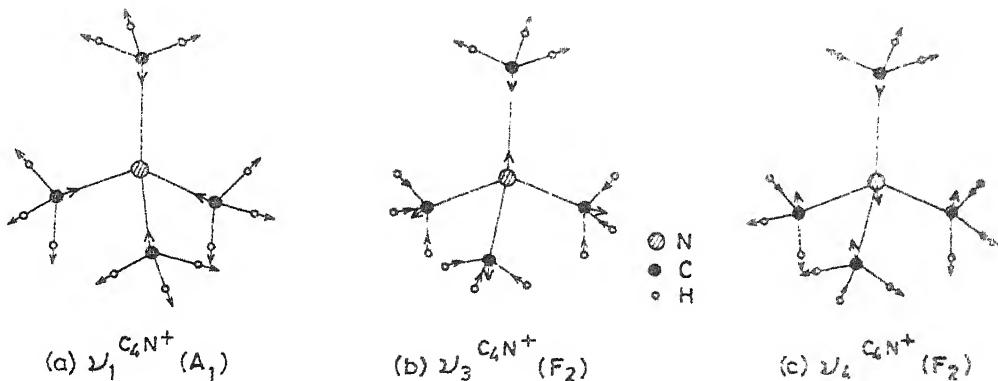


Fig. 3-5 Diagrammatic representation of three totally symmetric CH-stretching motions of  $\text{CH}_3$  in tetramethyl ammonium ion. (a) The  $\text{T}_d$  symmetry is retained, (b) and (c) the symmetry will be dynamically distorted to  $\text{C}_{3v}$  (cf. column 3 in table 3-6)

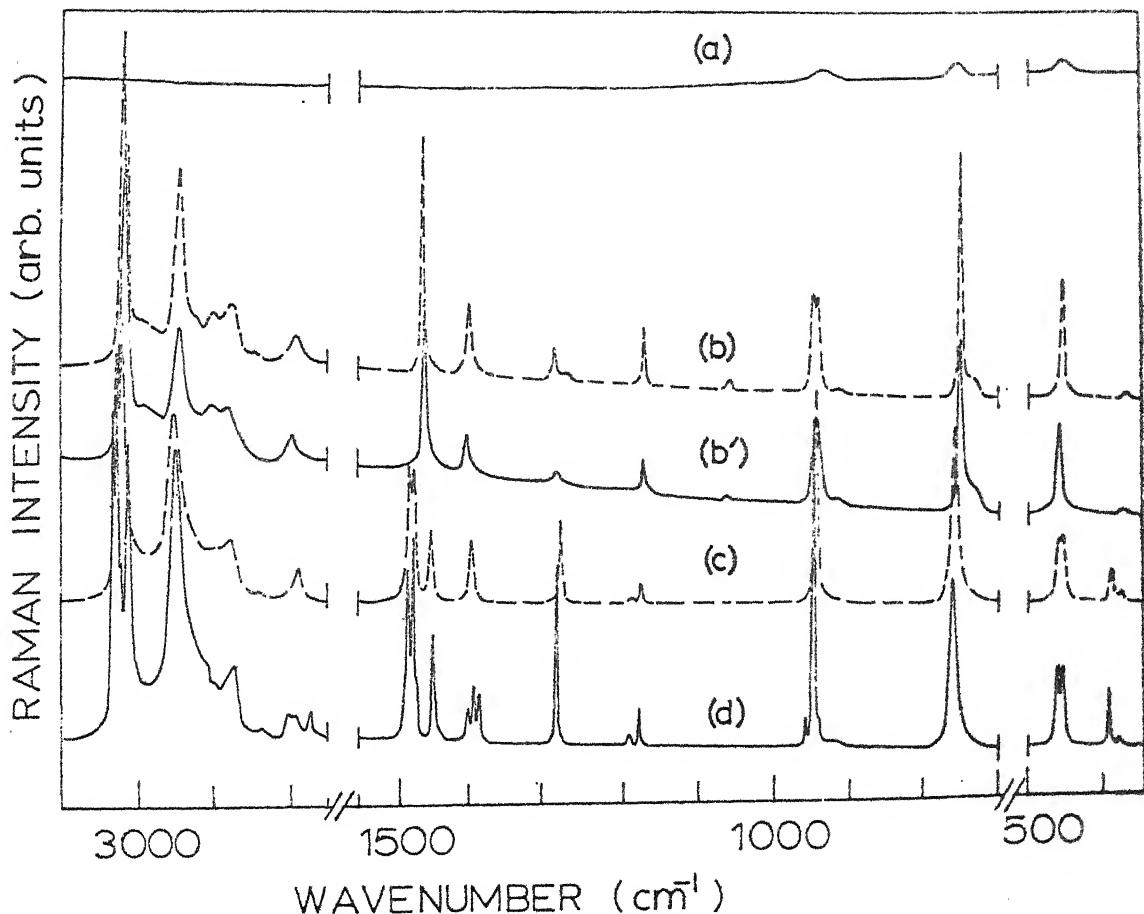


Fig. 3-6 Raman spectra of TMA Cl-d0 in four phases: (a) in phase I at 540 K (b) in phase II at 393 K (b') in phase II at 300 K after cooling under vacuum (c) in phase III at 300 K and (d) in phase IV at 90 K.

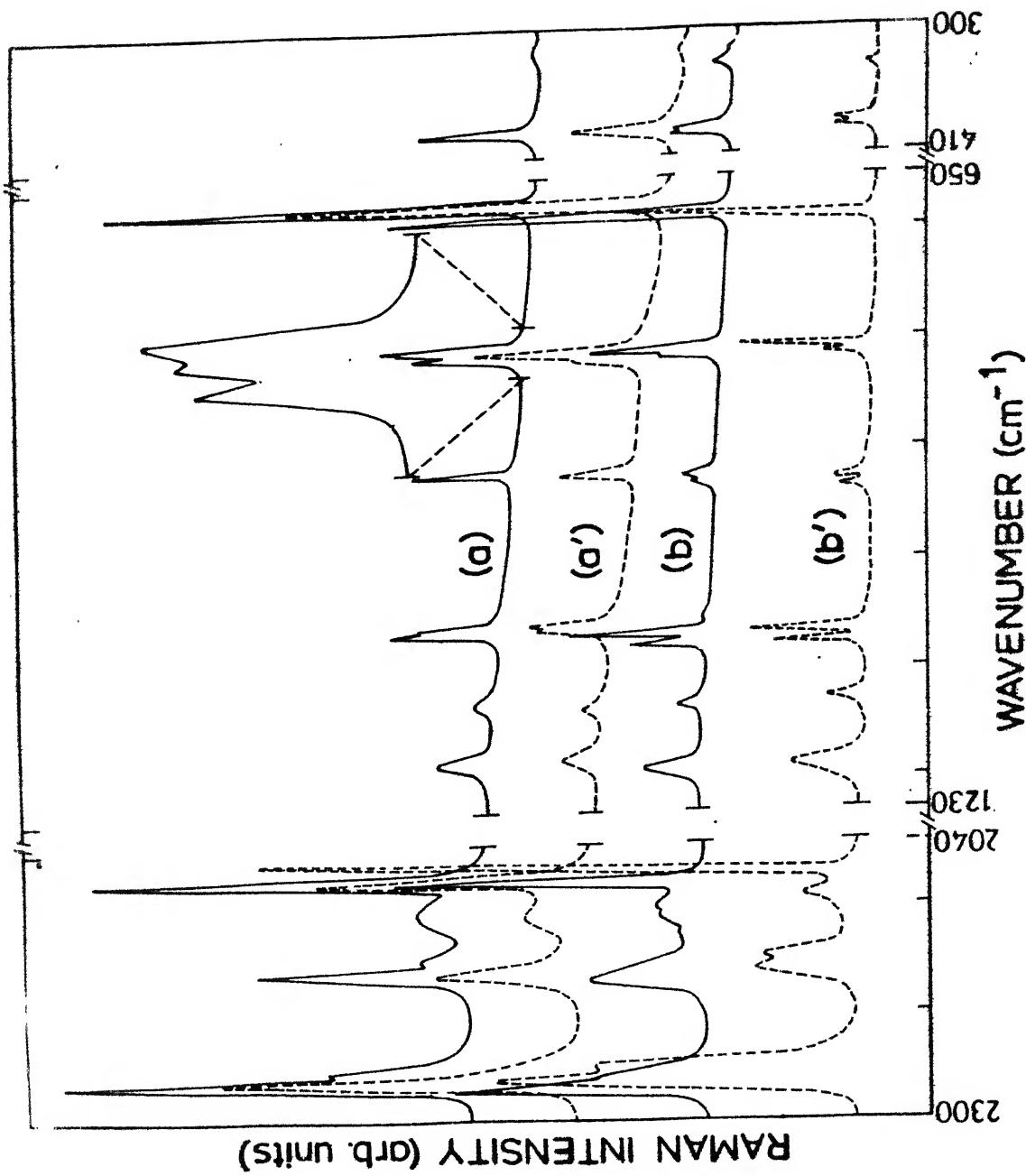


Fig. 3.7 Raman spectra of TMACl-d<sub>12</sub> : (a) Phase II, at 433 K, (a') Phase II at 300 K - on cooling under vacuum, (b) Phase III at 300K and (b') Phase III at 90 K.

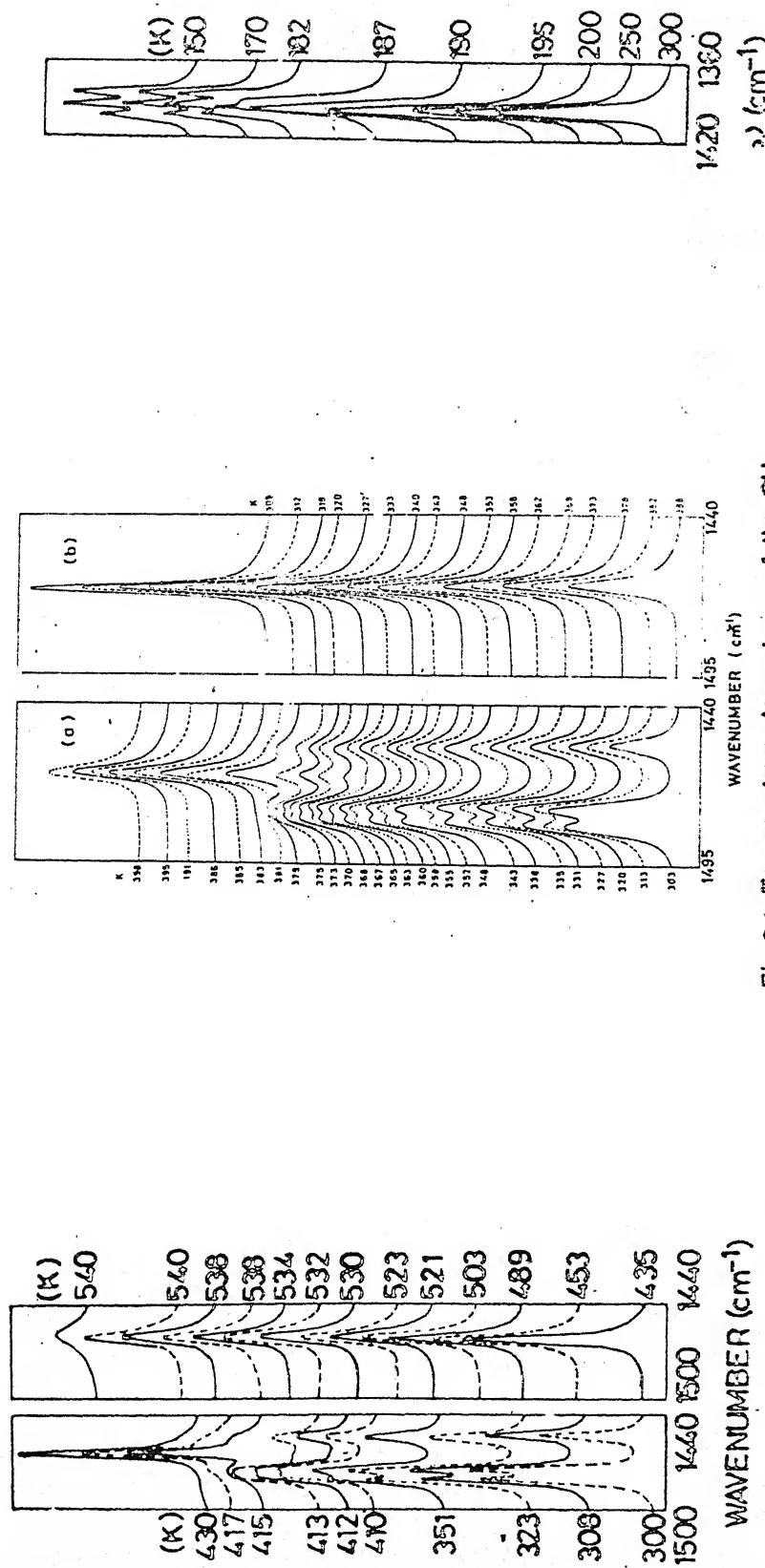


Fig. 3.8 Temperature dependence (in the range 300-540 K) of  $\nu_6$  and  $\nu_{15}$  modes of  $\text{CH}_3$  in TMA ion for determining the phases transitions III  $\rightarrow$  II  $\rightarrow$  I (without vacuum).

Fig. 3.9: Temperature dependence of the  $\text{CH}_3$  antisymmetric deformations,  $\nu_6(E)$  and  $\nu_{15}(F_2)$  in TMA-Cl<sub>3</sub> for determining the III  $\rightarrow$  II phase transition under vacuum (a) heating cycle and (b) cooling cycle.

Fig. 3.10 Temperature dependence (in the range 300-150 K) of  $\nu_{16}$  mode of  $\text{CH}_3$  in TMA ion for determining the phase transition III  $\rightarrow$  IV.

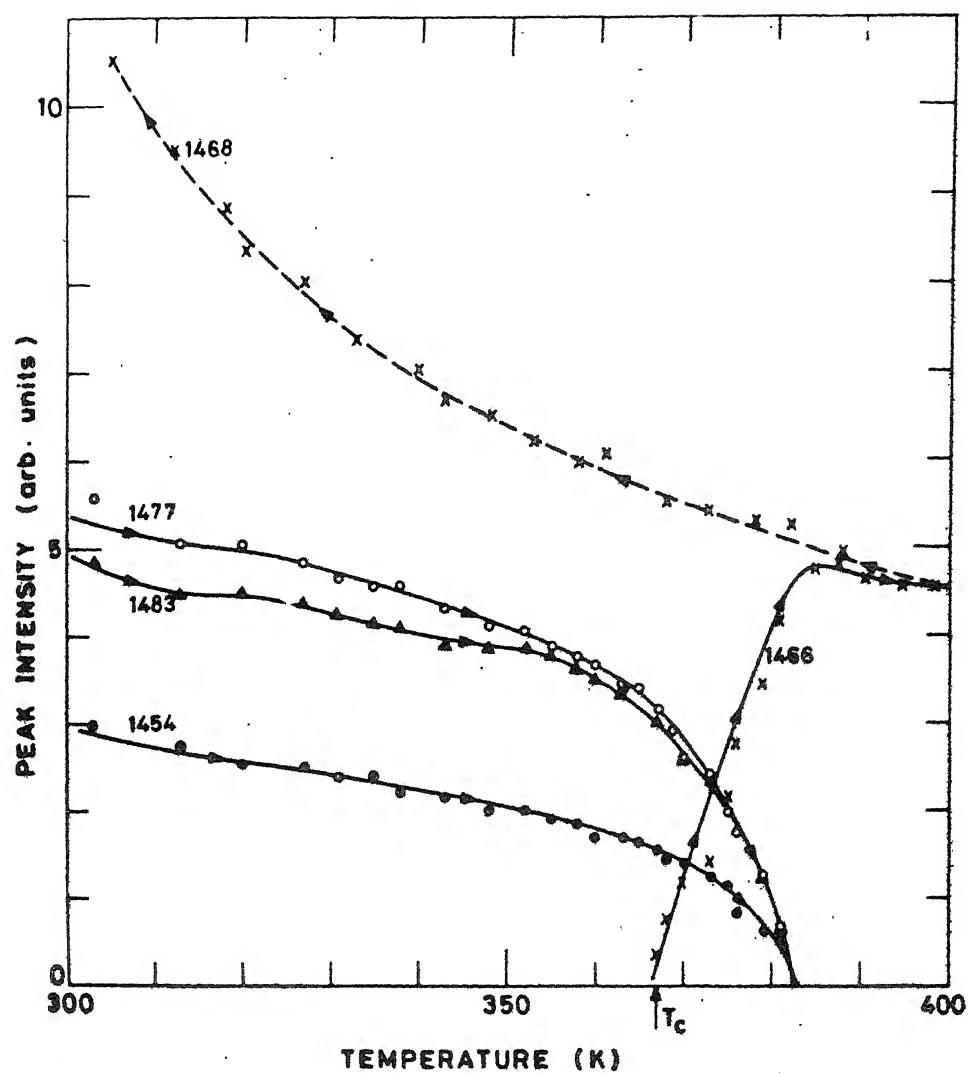


Fig. 3.11 The variation of peak intensities of  $\nu_6(E)$  at  $1454\text{ cm}^{-1}$  and  $\nu_{15}(F_2)$  at  $1477$  and  $1483\text{ cm}^{-1}$  in TMAC- $d_0$  with temperature. The phase transition III  $\rightarrow$  II is characterized by the appearance of a new band at  $1466\text{ cm}^{-1}$ . On cooling the sample from  $400\text{ K}$  the band gains intensity.

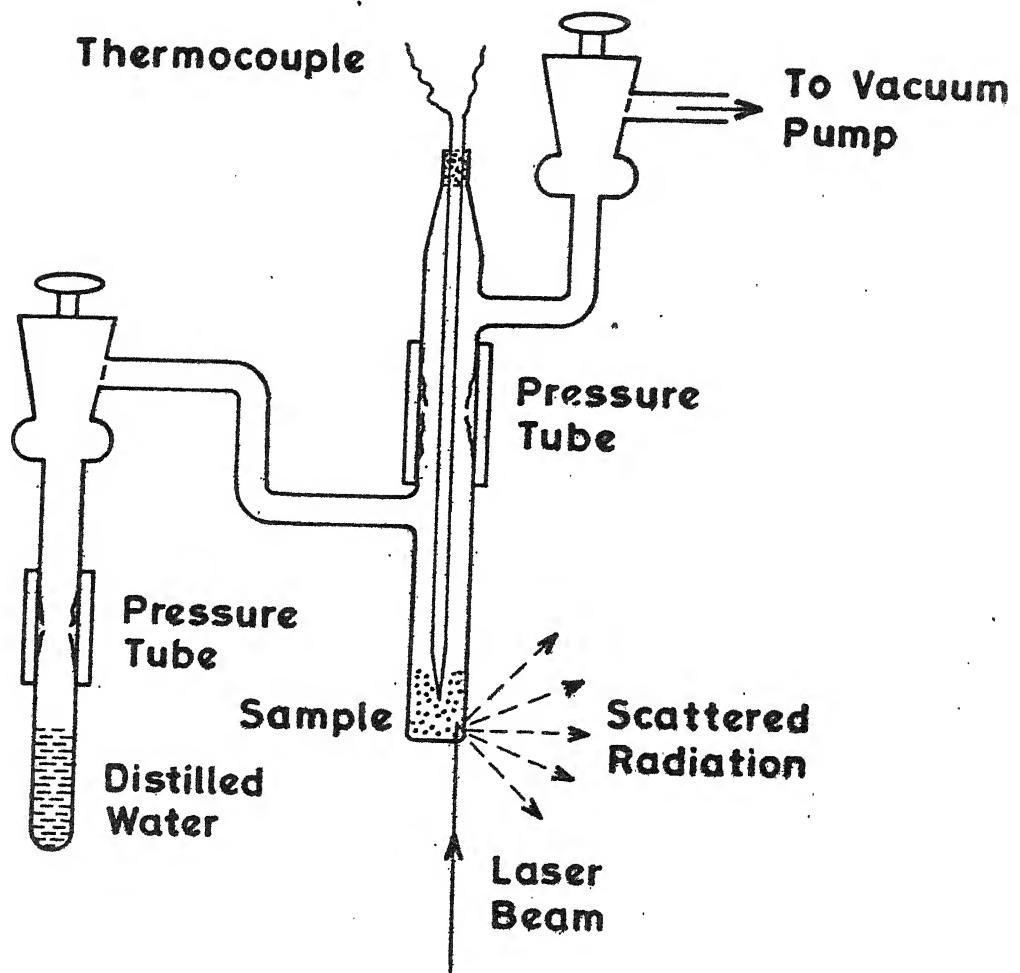


Fig.3.12 Sample Holder (for High Temperature Cell) having an Arrangement to Flow Water Vapour Over the Sample Under Vacuum.

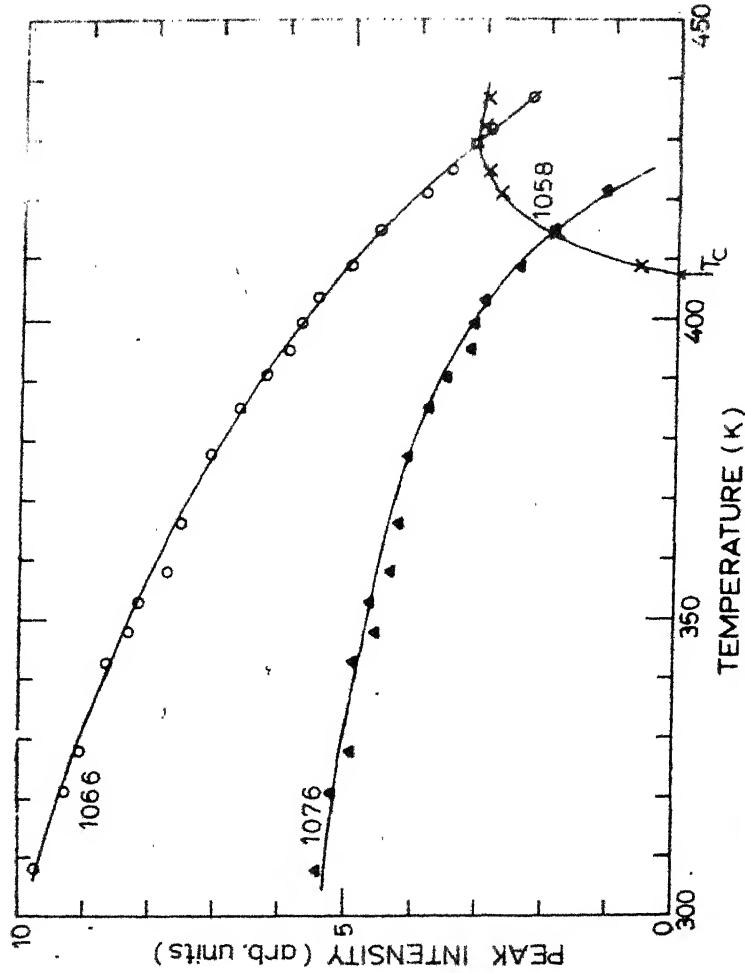


Fig.3.14 The variation of peak intensities of  $\nu_{15}(F_2)$  at 1066 and 1076  $\text{cm}^{-1}$  in TMAC- $d_{12}$  with temperature. The phase transition III  $\rightarrow$  II is characterized by the appearance of a new band at  $1058 \text{ cm}^{-1}$ .

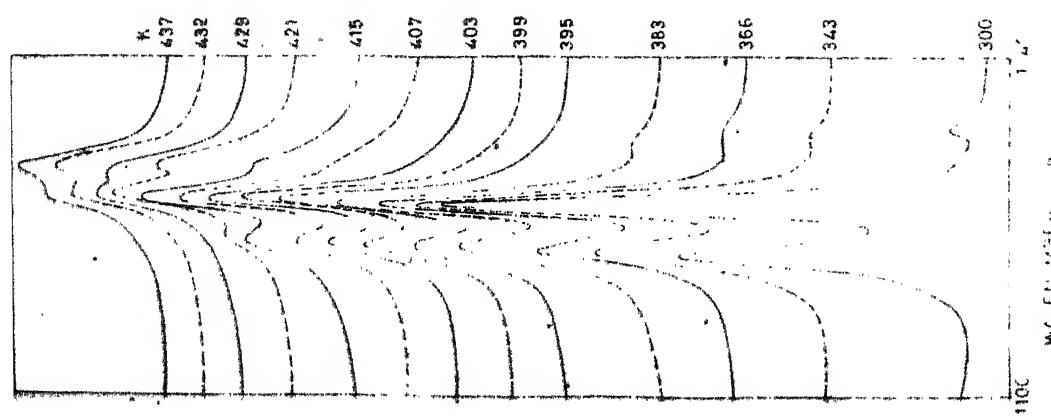


Fig.3.13 Temperature dependence of the  $\text{CD}_3$  antisymmetric deformations,  $\nu_6(\text{E})$  and  $\nu_{15}(F_2)$  in TMAC- $d_{12}$  for determining the phase transition III  $\rightarrow$  II (under vacuum).

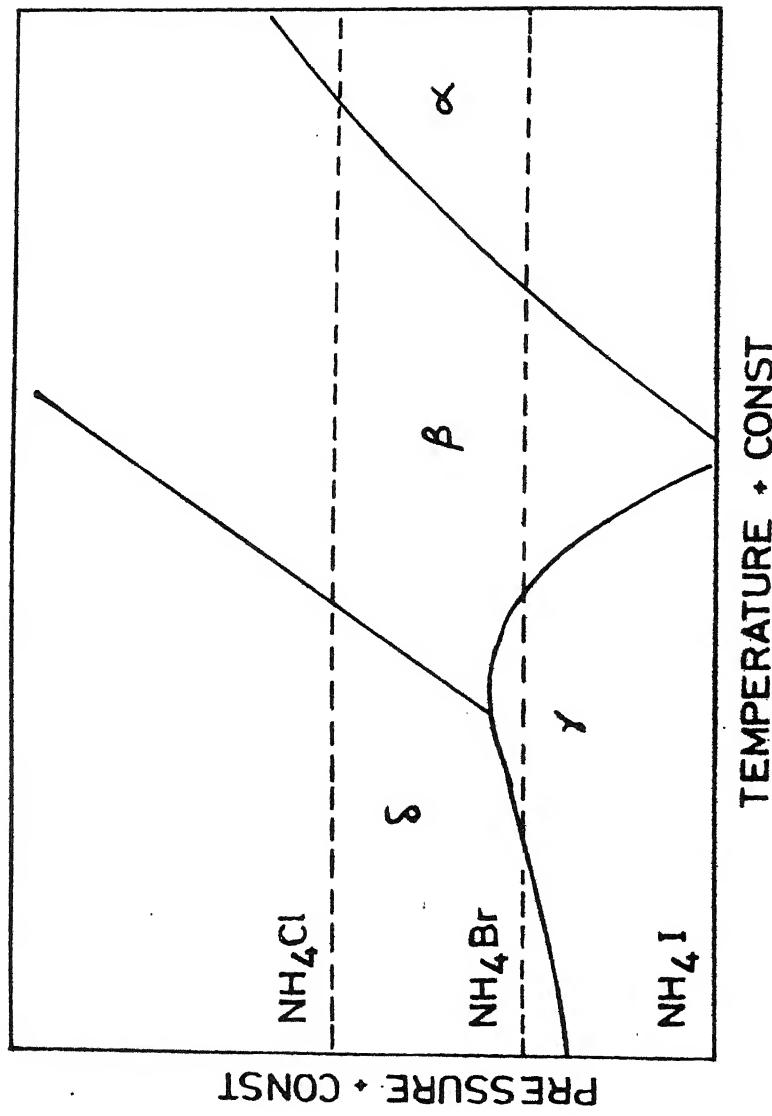


Fig. 3.15 Schematic generalized phase diagram of ammonium halides [7]

#### 4. VIBRATIONAL STUDIES OF TETRAMETHYL AMMONIUM BROMIDE AND IODIDE

In this chapter we present the temperature dependent Raman studies of normal ( $d_0$ ) tetramethyl ammonium bromide and iodide. These studies provide information about the specific molecular motions involved in the phase transitions [1]. For example, the C-N vibrational bands would be affected mainly by the reorientational motions of the whole TMA ion, the bands of  $CH_3$  groups would change only if the motions of the methyl groups are affected, and a splitting of the totally symmetric stretching mode of  $C_4N$  skeleton [ $\nu_3(A_1)$ ] will indicate orientational disorder of the TMA ion. Raman data for selectively deuterated tetramethyl ammonium iodide ( $TMAI-d_n$ ;  $n = 0, 1, 3, 9, 10, 11$  and 12) at room temperature are also presented in this chapter.

##### 4.1 CRYSTAL STRUCTURE AND GROUP THEORETICAL ANALYSIS

TMA halides at room temperature belong to the tetragonal system with space group  $D_{4h}^7$  ( $z = 2$ ) [2,3]. It is useful to recall Ohe's proposal [4] of four types of structures for  $(TMA)_2XCl_6$  ( $X = U$  or  $Sn$ ) which belong to the cubic system. The four structure arise from the  $2 \times 2$  alternatives provided by

- (i) staggered and eclipsed configurations of the methyl groups of a TMA ion, and
- (ii) parallel and perpendicular orientations of TMA ion.

For a cubic system, viz.  $(TMA)_2XCl_6$ , the two orientations are defined as N-C bonds pointing towards the corners of the cube occupied by the X atoms (parallel orientation) and the bonds pointing towards the vacant corners (perpendicular orientation) [4]. The parallel and perpendicular orientations for TMA halides are shown in Fig. 4.1. Since TMA halides belong to the tetragonal system, the equilibrium orientations for these will be somewhat different from the parallel and perpendicular orientations of a cubic system. Yet the terms may be used to give a close enough description of mutual orientation in the four possible structures.

The forty-five internal modes of TMA ion under point group  $T_d$  are distributed as  $3A_1 + A_2 + 4E + 4F_1 + 7F_2$  and are represented as  $\nu_1, \nu_2, \dots, \nu_{19}$  [see chap. 3]. The modes may further split due to correlation field under the known space group  $D_{4h}^7$  ( $Z = 2$ ) through site symmetry  $D_{2d}$  (in case both the TMA ions occupy the same site). Then

$$\begin{aligned}
 \text{vib}^{TMA} = & 7A_{1g}(R) + 4A_{2g} + 7B_{1g}(R) + 5B_{2g}(R) + 11E_g(R) \\
 & + 5A_{1u} + 7A_{2u}(IR) + 4B_{1u} + 7B_{2u} + 11E_u(IR)
 \end{aligned} \quad (4.1)$$

It is seen that each of the nineteen modes of isolated TMA produces at least one Raman active (g) species under the

space group  $D_{4h}^7$ . Hence for a polycrystalline sample all these modes are expected to appear in the Raman spectrum.

#### 4.2 CHARACTERISTIC RAMAN SPECTRA OF NORMAL ( $d_0$ ) TMABr AND TMAI AT 300 AND 100 K

The relevant portions of the observed Raman spectra of normal ( $d_0$ ) TMABr and TMAI in the region 200-4000  $\text{cm}^{-1}$  are shown in Figs. 4.2 and 4.3, respectively. The peak positions of the observed bands and their assignments are given in Table 4.1. Positionwise, the observed spectra fit well into the assignment proposed earlier for TMACl (which are also given for comparison in Table 4.1). Hence the assignment aspect does not merit further discussion.

#### 4.3 DYNAMIC DISORDER OF TMA ION IN NORMAL ( $d_0$ ) TMA HALIDES

The temperature dependent Raman spectra in the  $C_4^N$  symmetric stretching region (735 to 765  $\text{cm}^{-1}$ ) of normal ( $d_0$ ) TMAI are shown in Fig. 4.4. The room temperature spectrum shows two bands in this region at 748 and 753  $\text{cm}^{-1}$ . On lowering the temperature the former band gains intensity and shifts to 746  $\text{cm}^{-1}$  whereas the later does not show an appreciable change in intensity but shifts to 758  $\text{cm}^{-1}$ . In case of TMACl and TMABr, too, two bands appear at 730 and 760  $\text{cm}^{-1}$  and at 724 and 757  $\text{cm}^{-1}$ , respectively. Out of these the lower frequency member is very weak. The main band (at 760  $\text{cm}^{-1}$  in TMACl and 757  $\text{cm}^{-1}$  in TMABr) has been assigned

to the  $\nu_3(A_1)$  mode while the weak one is assigned to the overtone of  $\nu_8(E)$ . In TMAI, the  $\nu_8(E)$  mode has negligible intensity and its position could not be sorted out from the spectra; the overtone would be even weaker. The observed  $748 \text{ cm}^{-1}$  band has good intensity, particularly so at low temperatures. Therefore the  $748 \text{ cm}^{-1}$  band in TMAI cannot be an overtone of the  $\nu_8(E)$  mode. If one considers the band at  $753 \text{ cm}^{-1}$  as an overtone of  $\nu_8(E)$  assuming that its intensity is due to Fermi resonance with  $748 \text{ cm}^{-1}$  band, then the assignment becomes untenable due to the following reasons :

- (i) in the cases of TMACl and TMABr the overtone of  $\nu_8(E)$  falls at 730 and  $724 \text{ cm}^{-1}$ , respectively,
- (ii) the increase in intensity of  $748 \text{ cm}^{-1}$  band on going to lower temperatures would then suggest a decrease in Fermi resonance interaction, while the observed opposite shifts of the two bands (to 746 and  $758 \text{ cm}^{-1}$  at 100 K) would suggest an enhancement in Fermi resonance interaction.

The above discussion leads to the idea that neither of the two bands in the stretching region of TMAI spectra can be an overtone of  $\nu_8(E)$ . The only other alternative is that these are the two components of  $\nu_3(A_1)$ . On the other hand, factor group analysis suggests that although a mode of species  $A_1$  under the point group symmetry  $T_d$  may split into two components under the space group  $D_{4h}^7$  through the site

symmetry  $D_{2d}$ , only one of them would be Raman active. In a vibrational spectrum some of the bands might be missing because of either lack of intensity or accidental degeneracy, but the appearance of extra bands contrary to the spectral model is unacceptable. The two observed Raman components of  $\nu_3(A_1)$  in TMAI could therefore be explained only in terms of a model with two different sites for TMA ions in the lattice which could arise on account of parallel and perpendicular orientations of TMA ions (cf. Fig. 4.1). The model is discussed in section 4.3.1.

The  $\text{CH}_3$  asymmetric deformation mode  $\nu_{15}(F_2)$  (cf. Table 4.1) also needs attention. It shows only two components at room temperature in TMACl and TMABr, whereas it has three components in TMAI. The splitting of  $\nu_{15}(F_2)$  into three components in TMAI is again contrary to the group theoretical prediction. On lowering the temperature, the  $\nu_{15}(F_2)$  mode in TMABr also splits into three components at 182 K (Fig. 4.5). However, the temperature behaviour of the three components in TMABr and TMAI are not the same. It is thus obvious that the structure of TMAI at room temperature is different from that of TMABr and TMACl, although X-ray studies have not been able to record this difference and have shown that all the three salts are isostructural [2, 3].

In TMACl the modes belonging to the  $\text{CH}_3$  groups and  $\text{C}_4\text{N}$  skeleton are found to be thermosensitive [Chap. 3]. Since Tench [5] has shown from X-ray studies that phase IV

of TMACl (184.9 K to 75.8 K) has nearly the same structure (tetragonal) and dimensions as those in the room temperature phase III, the transition III  $\rightarrow$  IV is attributed to a change in reorientational freedom of the TMA ion [6]. Nuclear magnetic relaxation studies [6-10] have shown that  $\text{CH}_3$  reorientation and tumbling of TMA ion occurs in TMA halides. Chang et al. [11] have suggested that the phase transition III  $\rightarrow$  IV in TMACl may involve motion of TMA ion in the free space available inside the lattice. If this holds then tumbling motion of TMA ion should depend directly on the free space available in the crystal lattice. The data of Table 4.2 clearly show that the free space available for TMA ion in the unit cell is larger in TMAI than that in TMABr and TMACl. Thus the TMA ion is relatively more free to tumble in TMAI. This explains why the  $\text{C}_4\text{N}$  skeleton bands show considerable thermosensitivity in TMAI.

#### 4.3.1 Pseudo-double Well Potential Model

Let us assume a pseudo-double well potential [12,13] with different levels of their potential minima. The energy difference of the minima can be derived from the slope  $m$  of  $\ln (I_1/I_2)$  versus  $1000/T$  curve (Fig. 4.6) using Boltzmann statistics. Here  $I_1/I_2$  is the intensity ratio of the two component bands and equals the occupation ratio of the two sites. This leads to

$$\frac{I_1}{I_2} = \frac{n_1}{n_2} = C \exp \left( - \frac{\Delta E}{RT} \right) \quad (4.2)$$

where C is a constant,  $\Delta E$  is energy difference in molar units and R is the gas constant. The slope m of the dotted line in Fig. 4.6 gives

$$\Delta E = - 1000 \text{ mR} \quad (4.3)$$

The observed slope in the TMAI case leads to  $\Delta E = 0.43 \text{ KCal mol}^{-1}$ . The deviation of the curve from straight line at the low temperature end may be due to the dominance of temperature dependent flip-flop relaxation [12]. Since the components are overlapping and the half-widths of the bands are of the order of the slit-width, the value of difference between the two potential minima can only be treated as a broad estimate.

#### 4.4 RAMAN SPECTRA OF SELECTIVELY DEUTERATED TETRAMETHYL AMMONIUM IODIDE

The Raman spectra of the polycrystalline TMAI-d<sub>n</sub> ( $n = 0, 1, 3, 9, 10, 11$  and 12) at room temperature are shown in Fig. 4.7. The observed band-positions along with their vibrational assignment are given in Table 4.3. The assignment is done under the point group symmetry T<sub>d</sub> for TMA ion, neglecting the possible distortion in this symmetry on isotopic substitution and correlation field splittings. The spectra of TMAI-d<sub>0</sub> and -d<sub>12</sub> differ from those of the corresponding Cl analogues only in the additional splittings of a few of the bands. The assignment of the bands for TMAI-d<sub>0</sub> has been

discussed earlier in sec. 4.2 and that for TMAI-d<sub>12</sub> conveniently follows from a comparison with the spectrum of TMACl-d<sub>12</sub> (cf. sec. 3.6). The assignment of bands in TMAI-d<sub>n</sub> (n = 1, 3, 9, 10 and 11) is, however, not straight-forward. The details of the band assignments are discussed below.

#### 4.4.1 Modes of C<sub>4</sub>N Skeleton

The band-positions of the four internal modes of C<sub>4</sub>N skeleton are well known. The symmetric stretching mode,  $\nu_3$  (A<sub>1</sub>) appears as a strong band at 748 cm<sup>-1</sup> in TMAI-d<sub>0</sub>, with a weak shoulder at 753 cm<sup>-1</sup>. In the deuterated samples, TMAI-d<sub>n</sub> we find a single strong band in each sample, which shifts to 743, 737, 695, 688, 682 and 678 cm<sup>-1</sup> with n = 1, 3, 9, 10, 11 and 12, respectively in TMAI-d<sub>n</sub>. The two-fold splitting of this band in d<sub>0</sub> salt has been ascribed to the dynamic disorder of TMA ion. The appearance of this band as a singlet in the deuterated salts may be due to two counts : (i) the D for H substitution causes a decrease in the splitting, and (ii) the TMA ion is less disordered in the deuterated salts. The asymmetric stretch,  $\nu_{18}$  (F<sub>2</sub>), which appears as a single strong band at 940 cm<sup>-1</sup> in d<sub>0</sub> sample, appears as a single band also in d<sub>12</sub> but at 806 cm<sup>-1</sup>. This is as expected, because the symmetry is not changed, and mass effect would decrease  $\nu$ . In the intermediate samples the band, however, shows a multiplet structure, three components being identified in each case. This is

expected because of different distributions of D's among the four methyl groups. We note that with increasing n the intensity weighted frequency shifts monotonously to lower values and that the intensity distribution varies among the components. The asymmetric deformation mode,  $\nu_{19}(F_2)$  appears as a doublet for  $d_0$ ,  $d_3$ ,  $d_{11}$  and  $d_{12}$  salts, while as a triplet for  $d_1$ ,  $d_9$  and  $d_{10}$  salts. The band-positions are as given in Table 4.3. The symmetric deformation mode,  $\nu_5(E)$  could not be observed in any of these compounds. The intensity distribution among various component bands of the degenerate modes vary anomalously from one salt to the other. The appearance of the asymmetric bands as doublets for some of the partially deuterated salts may be due to very weak intensity of their third component or the two components falling together.

#### 4.4.2 Deformation and Librational Modes of Methyl Group

The rocking mode of methyl group,  $\nu_7(E)$  has been observed at 1172 and  $923\text{ cm}^{-1}$  in TMAI- $d_0$  and TMAI- $d_{12}$ , respectively, exhibiting a frequency shift ratio of 1.27. Thus frequency shift ratios of  $\sim 1.18$  and  $\sim 1.09$  are expected for the analogous rocking modes of  $\text{CHD}_2$  and  $\text{CH}_2\text{D}$  groups, respectively. Therefore, the band at  $958\text{ cm}^{-1}$  in TMAI- $d_{11}$  is assigned to  $\nu_7^{CHD_2}(E)$  and those at  $1016\text{ cm}^{-1}$  in TMAI- $d_{10}$  and  $1000\text{ cm}^{-1}$  in TMAI- $d_1$  to  $\nu_7^{CH_2\text{D}}(E)$ . The band at

$1000 \text{ cm}^{-1}$  in  $\text{TMAI-d}_1$ , however, seems to have some additional contribution from a split component of  $\nu_{18}(\text{F}_2)$ . Another methyl rocking mode  $\nu_{17}(\text{F}_2)$  shows a deuteration shift ratio of 1.28 ( $1282 \text{ cm}^{-1}$  in  $\text{TMAI-d}_0$  and  $1184 \text{ cm}^{-1}$  in  $\text{TMAI-d}_{12}$ ), fixing the frequency of  $\nu_{17}(\text{F}_2)$  to be around  $1245 \text{ cm}^{-1}$  which is indeed observed in  $\text{TMAI-d}_1$  but there is no evidence of this band in  $\text{TMAI-d}_{10}$ . Therefore this band ( $1246 \text{ cm}^{-1}$ ) and two other bands ( $1260$  and  $1292 \text{ cm}^{-1}$ ) in  $\text{TMAI-d}_1$  are assigned to the split components of  $\nu_{17}(\text{F}_2)$  due to the distortion of TMA ion from  $T_d$  symmetry on replacing one H by D. The asymmetric deformation of methyl group,  $\nu_6(\text{E})$  and  $\nu_{15}(\text{F}_2)$  are difficult to identify separately in the deuterated salts because of the strong mixing of these bands. Therefore, the four bands at  $1058$ ,  $1066$ ,  $1072$  and  $1078 \text{ cm}^{-1}$  in  $\text{TMAI-d}_{12}$  are jointly assigned to  $\nu_6(\text{E})$  and  $\nu_{15}(\text{F}_2)$  of  $\text{CD}_3$  group. Thus the frequency shift ratio for these bands on complete deuteration turns out to be  $\sim 1.37$  which implies a frequency shift ratio of  $\sim 1.12$  and  $\sim 1.24$  for  $\text{CH}_2\text{D}$  and  $\text{CHD}_2$  rock modes, respectively. Therefore, the bands at  $1334$  in  $\text{TMAI-d}_1$ , and at  $1318$  and  $1328 \text{ cm}^{-1}$  in  $\text{TMAI-d}_{10}$  are easily assigned to asymmetric deformations of  $\text{CH}_2\text{D}$  group and the band at  $1174 \text{ cm}^{-1}$  in  $\text{TMAI-d}_{11}$  to asymmetric deformation of  $\text{CHD}_2$  group. In  $\text{TMAI-d}_0$  the symmetric deformation mode  $\nu_{16}(\text{F}_2)$  appears as a strong band at  $1397 \text{ cm}^{-1}$  but  $\nu_2(\text{A}_1)$  does not appear at all. The case is inverted for  $\text{TMAI-d}_{12}$  where  $\nu_2(\text{A}_1)$  appears at  $1132 \text{ cm}^{-1}$ , though not very strong, but  $\nu_{16}(\text{F}_2)$  does

not appear. The bands at 1405, 1402 and  $1416\text{ cm}^{-1}$  in TMAI- $d_1$ ,  $-d_3$  and  $-d_9$ , respectively, are assigned to the  $\nu_{16}(F_2)$  mode of  $\text{CH}_3$  group. The weak doublet at 1310,  $1334\text{ cm}^{-1}$  in TMAI- $d_{11}$  is tentatively assigned to a component of  $\nu_{16}(F_2)$  due to  $\text{CHD}_2$  group which needs verification, may be with the help of the spectrum of TMAI- $d_2$ . The bands at 1150, 1118 and 1108 and  $1117\text{ cm}^{-1}$  in TMAI- $d_3$ ,  $-d_9$ ,  $-d_{10}$  and  $-d_{11}$ , respectively, are by analogy assigned to the  $\nu_2(A_1)$  mode.

#### 4.4.3 Methyl Stretching Region

There are a number of bands in the methyl stretching region including four fundamentals. The assignments in TMAI- $d_0$  and  $-d_{12}$  conveniently follow from the comparison of spectra with those of TMACl- $d_0$  and  $-d_{12}$  [cf. Chap. 3] and are shown in Tables 4.1 and 4.3. The bands in TMAI- $d_1$ ,  $-d_3$ ,  $-d_9$ ,  $-d_{10}$  and  $-d_{11}$  having the band shapes similar to the bands in TMAI- $d_0$  and  $-d_{12}$  in the respective regions ( $\text{CH}_3$  or  $\text{CD}_3$  as the case may be) are tentatively assigned to the same bands as in latter salts, though there might be minor variations in the positions of some of the bands. This minor frequency variation is expected due to a variation in the intramolecular coupling on account of different D substituents. A few bands in  $d_1$ ,  $d_{10}$  and  $d_{11}$  salts are differently assigned. In  $d_1$  and  $d_{10}$ , there is one  $\text{CH}_2\text{D}$  group while the rest are either all  $\text{CH}_3$  groups or all  $\text{CD}_3$  groups. The  $\text{CH}_2\text{D}$  group would give rise to one uncoupled C-D stretch, and to one symmetric and one asymmetric stretching

modes of  $\text{CH}_2$ . Therefore the bands at 2968 and  $3010 \text{ cm}^{-1}$  in TMAI- $d_{10}$  are unambiguously assigned to  $\nu_{\text{sym.}}^{\text{CH}_2\text{D}}$  and  $\nu_{\text{asym.}}^{\text{CH}_2\text{D}}$  stretching modes, respectively. In TMAI- $d_1$ , the band at  $2970 \text{ cm}^{-1}$  is assigned to  $\nu_{\text{sym.}}^{\text{CH}_2\text{D}}$  stretch whereas the  $\nu_{\text{asym.}}^{\text{CH}_2\text{D}}$  stretch could not be observed separately because of overlapping bands of  $\nu_5(\text{E})$  and  $\nu_{13}(\text{F}_2)$  modes of  $\text{CH}_3$  group. In the  $\text{CD}_3$  stretching region for TMAI- $d_1$ , only one band that due to uncoupled C-D stretch is expected. However, we observe two bands at 2194 and  $2223 \text{ cm}^{-1}$ . The doublet may arise due to the reasons: (i) the bond lengths of C-H bonds in  $\text{CH}_3$  may be nonequivalent, and (ii) one band is due to C-D stretch while the other is some combination or overtone. The solution spectrum supports the later possibility where two bands in this region are observed. Therefore the band at  $2223 \text{ cm}^{-1}$  is assigned to  $\nu(\text{C-D})$  whereas the other could be some two-phonon band and is left unassigned. Similarly, in TMAI- $d_{10}$  the band at  $2220 \text{ cm}^{-1}$  is assigned to  $\nu(\text{C-D})$ . TMAI- $d_{11}$  has one  $\text{CHD}_2$  group and the rest  $\text{CD}_3$  groups. We, therefore, expect an uncoupled C-H stretching band in the  $\text{CH}_3$ -region and two bands in the  $\text{CD}_3$  region (one symmetric stretch and one asymmetric stretch of  $\text{CD}_2$ ) of  $\text{CHD}_2$  group apart from the modes of  $\text{CD}_3$  group. The single band at  $2984 \text{ cm}^{-1}$  in the  $\text{CH}_3$  stretching region is unambiguously assigned to  $\nu(\text{C-H})$ . The band at  $2174 \text{ cm}^{-1}$  is conveniently assigned to  $\nu_{\text{sym.}}^{\text{CHD}_2}$  whereas the  $\nu_{\text{asym.}}^{\text{CH}_2\text{D}}$  band is overlapped by the  $\nu_5(\text{E})$  (or  $\nu_{13}(\text{F}_2)$ ) mode of  $\text{CD}_3$ . In TMAI- $d_9$ , we observed some unexpected additional weak bands having positions very near to the ones in TMAI- $d_1$ .

It is, therefore, suspected that small traces of TMAI-d<sub>1</sub> were present in TMAI-d<sub>9</sub> as impurity.

#### 4.5 CONCLUSION

The spectral evidence shows that TMACl-d<sub>0</sub> and TMABr-d<sub>0</sub> are isostuctural while TMAI-d<sub>0</sub> seems to possess a different structure at room temperature. This needs to be verified by the direct and conventional methods such as X-ray diffraction, inelastic neutron scattering etc. The free space available to TMA-d<sub>0</sub> ion in the unit cell is larger in the case of TMAI-d<sub>0</sub> than in TMACl-d<sub>0</sub> and TMABr-d<sub>0</sub> and the electronegativity of halide ion is less for TMAI-d<sub>0</sub>. These facts put together allows the TMA-d<sub>0</sub> ion in TMAI-d<sub>0</sub> to tumble more freely in two inequivalent orientational positions (parallel and perpendicular) leading to the splitting of the totally symmetric mode of C<sub>4</sub>N skeleton,  $\nu_3(A_1)$ . A tentative assignment of the vibrational modes of selectively deuterated TMA iodides is proposed on the basis of their room temperature Raman spectra. The distribution of intensity among various bands vary anomalously in the differently deuterated salts (TMAI-d<sub>n</sub>, n = 0, 1, 3, 9, 10, 11 and 12). The separation between methyl symmetric and asymmetric stretching modes also show anomalous behaviour being less in TMAI-d<sub>0</sub> than in TMAI-d<sub>12</sub>.

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Table 4.1 : Raman band-positions ( $\text{cm}^{-1}$ ) of tetramethyl ammonium halides (chloride, bromide and iodide) at room temperature and low temperature with their proposed assignments under point group symmetry  $T_d$  for  $(\text{CH}_3)_4\text{N}^+$  ion.

| TMACl-d <sub>0</sub> <sup>a</sup> |                  |                     |                     | TMABr-d <sub>0</sub> |                     | TMAI-d <sub>0</sub> |       | Assignment              |
|-----------------------------------|------------------|---------------------|---------------------|----------------------|---------------------|---------------------|-------|-------------------------|
| 300 K                             | 90 K             | 300 K               | 100 K               | 300 K                | 100 K               | 300 K               | 100 K |                         |
| 376                               | 376              | ....                | ....                | ....                 | ....                | ....                | ....  | $\nu_8(\text{E})$       |
| 388                               | 389              | 384w, b             | 392w                | ....                 | ....                | ....                | ....  |                         |
| 454                               | 456              | 450s                | 454s                | 449s                 | 451s                | ....                | ....  | $\nu_{19}(\text{F}_2)$  |
| 459                               | 464              | 460m                | 466m                | 460m                 | 464m                | ....                | ....  |                         |
| 730 <sup>b</sup>                  | 736 <sup>b</sup> | 724 <sup>b</sup> vw | 726 <sup>b</sup> vw | ....                 | ....                | ....                | ....  | $2\nu_8(\text{E})$      |
| 760                               | 758              | 757s                | 757s                | 748s                 | 746s                | ....                | ....  | $\nu_3(\text{A}_1)$     |
| ...                               | ...              | ....                | ....                | 753m                 | 758m                | ....                | ....  |                         |
| ...                               | 887 <sup>b</sup> | 916 <sup>b</sup> vw | 924 <sup>b</sup> vw | 916 <sup>b</sup> vw  | 920 <sup>b</sup> vw | ....                | ....  | $2\nu_{19}(\text{F}_2)$ |
| 930 <sup>b</sup>                  | 940              | ....                | ....                | ....                 | 938vw               | ....                | ....  | $\nu_{18}(\text{F}_2)$  |
| 948                               | 946              | 945vs               | 946vs               | 940vs                | 942vs               | ....                | ....  |                         |
| ...                               | 958              | ....                | ....                | ....                 | ....                | ....                | ....  |                         |
| 1182                              | 1183             | 1180w, b            | 1183w               | 1172w, b             | 1176w, b            | ....                | ....  | $\nu_7(\text{E})$       |
| 1192                              | 1197             | ....                | ....                | ....                 | ....                | ....                | ....  |                         |
| ...                               | ....             | ....                | ....                | 1278vw               | 1280w               | ....                | ....  | $\nu_{17}(\text{F}_2)$  |
| 1286                              | 1291             | 1284s               | 1286s               | 1282s                | 1285s               | ....                | ....  |                         |
| 1398                              | 1392             | 1394sh              | 1393sh              | ....                 | ....                | ....                | ....  | $\nu_{16}(\text{F}_2)$  |
| 1402                              | 1397             | 1399s               | 1396s               | 1397vs               | 1395vs              | ....                | ....  |                         |
| ...                               | 1407             | ....                | ....                | ....                 | ....                | ....                | ....  |                         |
| 1454                              | 1452             | 1451m               | 1449m               | 1448m                | 1447m               | ....                | ....  | $\nu_6(\text{E})$       |
| ...                               | 1474             | ....                | 1468w               | 1465m                | 1466m               | ....                | ....  |                         |
| 1477                              | 1479             | 1472s               | 1474s               | 1468s                | 1469s               | ....                | ....  | $\nu_{15}(\text{F}_2)$  |
| 1483                              | 1486             | 1477m               | 1480m               | 1471m                | 1471s               | ....                | ....  |                         |

| TMACl-d <sub>2</sub> <sup>a</sup> |                   |                      | TMABr-d <sub>2</sub> |                        | TMAI-d <sub>2</sub>    |                        | Assignment                      |
|-----------------------------------|-------------------|----------------------|----------------------|------------------------|------------------------|------------------------|---------------------------------|
| 300 K                             | 90 K              |                      | 300 K                | 100 K                  | 300 K                  | 100 K                  |                                 |
| ...                               | 2770              | ....                 | ....                 | ....                   | ....                   | ....                   |                                 |
| 2790                              | 2792              | 2786m                | 2780m                | 2783m                  | 2776m                  | 2776m                  | $\nu_{16}(F_2)$                 |
| ...                               | 2800              | ....                 | ....                 | ....                   | ....                   | 2780w                  |                                 |
| 2840                              | 2834              | 2840vw               | 2834vw               | 2834vw                 | 2828vw                 | 2828vw                 | $\nu_6(E) + \nu_{16}(F_2)$      |
| 2877                              | 2872              | 2872m, b             | 2868m, b             | 2868m                  | 2864m                  | 2864m                  | $\nu_{15}(F_2) + \nu_{16}(F_2)$ |
| 2900 <sup>b</sup>                 | 2900 <sup>b</sup> | 2893 <sup>b</sup> vw | 2886 <sup>b</sup> vw | 2892 <sup>b</sup> vw   | 2880 <sup>b</sup> vw   | 2880 <sup>b</sup> vw   | $\nu_6(E)$                      |
| 2918 <sup>b</sup>                 | 2920 <sup>b</sup> | 2912 <sup>b</sup> vw | 2912 <sup>b</sup> vw | 2914 <sup>b</sup> vw   | 2912 <sup>b</sup> vw   | 2912 <sup>b</sup> vw   | $\nu_{15}(F_2)$                 |
| 2951                              | 2950              | 2944vs               | 2944vs               | 2938vs                 | 2932vs                 | 2932vs                 | $\nu_1(A_1)$                    |
| 2985 <sup>b</sup>                 | 2986 <sup>b</sup> | ....                 | ....                 | 2973 <sup>b</sup> w, b | 2980 <sup>b</sup> w, b | 2980 <sup>b</sup> w, b | $\nu_{14}(F_2)$                 |
| 3019                              | 3012              | 3014vs               | 3016vs               | 3010s                  | 3009vs                 | 3009vs                 | $\nu_5(E)$                      |
| ...                               | 3022              | ....                 | ....                 | ....                   | ....                   | ....                   |                                 |
| 3027                              | 3028              | 3020vs               | 3021vs               | 3015vs                 | 3014vs                 | 3014vs                 | $\nu_{13}(F_2)$                 |
| ...                               | 3033              | ....                 | ....                 | ....                   | ....                   | ....                   |                                 |
|                                   |                   |                      |                      |                        |                        |                        |                                 |

<sup>a</sup>From chap. 3.

<sup>b</sup>The bands are very weak and broad or overlapping a strong band, so their positions may be uncertain to  $\pm 5 \text{ cm}^{-1}$ .

v - very, s - strong, m - medium, w - weak, sh - shoulder, b - broad.

Table 4.2 : Calculation of free space available in the unit cells of  $\text{TMACl-d}_0$ ,  $\text{TMABr-d}_0$  and  $\text{TMAI-d}_0$ ; all are tetragonal at room temperature having space group  $D_{4h}^7$  ( $z = 2$ ).

| Compound           | Unit cell dimension<br>$a(\text{\AA})^a$ | $c(\text{\AA})^a$ | Vol. unit cell<br>$(\text{\AA}^3)$ | Ionic radius of halide ion<br>$(\text{\AA})^b$ | Vol. occupied in unit cell by<br>Halide ions $(\text{\AA}^3)$ | Vol. occupied in unit cell by<br>TMA ions (and<br>free space) $(\text{\AA}^3)$ |
|--------------------|--|-------------------|------------------------------------|--|---|--|
| $\text{TMACl-d}_0$ | 7.78                                     | 5.53              | 334.72                             | 0.26   | 0.148   | 334.57   |
| $\text{TMABr-d}_0$ | 7.76                                     | 5.53              | 333.00                             | 0.39   | 0.497   | 332.50   |
| $\text{TMAI-d}_0$  | 7.941                                    | 5.749             | 362.53                             | 0.50   | 1.047   | 361.48   |

<sup>a</sup>Values taken from, J D H Donnay, Crystal Data, Am. Crystallogr. Assoc., 1963.

<sup>b</sup>Values taken from Table of Periodic Properties of the Elements, Sargent-Welch Scientific Com., Chicago, 1968.

Table 4.3 : Observed band-positions (in  $\text{cm}^{-1}$ ) in Raman spectra of selectively deuterated tetramethyl ammonium iodides (TMAI- $d_n$ ;  $d = 0, 1, 3, 9, 10, 11$  and 12) in polycrystalline form at room temperature with their assignment.

| $d_0$     | $d_1$    | $d_3$ | $d_9$ | $d_{10}$ | $d_{11}$ | $d_{12}$ | Assignment              |
|-----------|----------|-------|-------|----------|----------|----------|-------------------------|
| 449s      | 446m     | 438s  | 396m  | 390m     | 393s     | 382m     |                         |
| 460m      | 456m     | 454m  | 410m  | 396m     | 402m     | 390w     | $\nu_{19}(\text{F}_2)$  |
| ...       | 466m     | ...   | 416m  | 408m     | ...      | ...      |                         |
| ...       | 492w, br | ...   | ...   | ...      | ...      | ...      | ...                     |
| ...       | ...      | 720vw | 714w  | 694sh    | ...      | ...      | $2\nu_8(\text{E})$      |
| 748s      | 743s     | 737vs | 695vs | 688vs    | 682vs    | 678s     | $\nu_3(\text{A}_1)$     |
| 753m      | ...      | ...   | ...   | ...      | ...      | ...      |                         |
| 916vw     | ...      | ...   | ...   | ...      | ...      | ...      | $2\nu_{19}(\text{F}_2)$ |
| ...       | 875m     | 842m  | 811m  | 808s     | 806s     | 806s     |                         |
| 940vs     | 946s     | 934m  | 837m  | 850w     | 858w     | ...      | $\nu_{18}(\text{F}_2)$  |
| ...       | 1000w    | 994m  | 874m  | 868w     | ...      | ...      |                         |
| 1172vw, b | ...      | ...   | 955vw | 936vw    | 918vw    | 923vw    |                         |
| ...       | ...      | ...   | ...   | ...      | 958vw    | ...      | $\nu_7(\text{E})$       |
| ...       | 1000w    | ...   | ...   | 1016w    | ...      | ...      |                         |
| ...       | 1246w    | ...   | ...   | ...      | ...      | ...      |                         |
| 1278vw    | 1260w    | 1266m | 1194m | 1181s    | ...      | ...      | $\nu_{17}(\text{F}_2)$  |
| 1282s     | 1292w    | 1295w | 1249m | 1188s    | 1189s    | 1184s    |                         |
| 1397s     | 1405s    | 1402s | 1416w | ...      | ...      | ...      |                         |
| ...       | ...      | ...   | ...   | ...      | 1310vw   | ...      | $\nu_{16}(\text{F}_2)$  |
| ...       | ...      | ...   | ...   | ...      | 1334w    | ...      |                         |

Table 4.3 Contd....

| $d_0$  | $d_1$  | $d_3$  | $d_9$  | $d_{10}$ | $d_{11}$ | $d_{12}$ | Assignment                      |
|--------|--------|--------|--------|----------|----------|----------|---------------------------------|
| 1448m  | ...    | 1086w  | 1034w  | 1052vw   | ...      | 1058vw   |                                 |
| ...    | 1438w  | 1092w  | 1060vw | 1064w    | 1070m    | 1066w    |                                 |
| 1465m  | 1456w  | 1444m  | 1068w  | 1070vw   | 1080sh   | 1072w    | $\nu_6(E)$ or $\nu_{15}(F_2)$   |
| 1468s  | ...    | 1464w  | ...    | ...      | ...      | 1078vw   |                                 |
| 1471m  | 1472m  | 1469vw | ...    | ...      | ...      | ...      |                                 |
| ...    | ...    | 1478vw | 1472m  | ...      | ...      | ...      |                                 |
| ...    | ...    | ...    | ...    | ...      | 1174w    | ...      |                                 |
| ...    | ...    | ...    | ...    | 1318w    | ...      | ...      |                                 |
| ...    | 1334w  | ...    | ...    | 1328w    | ...      | ...      |                                 |
| ...    | ...    | ...    | ...    | 1446w, b | ...      | ...      | ...                             |
| ...    | ...    | 1150vw | 1118m  | 1108m    | 1117m    | 1132w    | $\nu_2(A_1)$                    |
| ...    | ...    | ...    | 2054sh | ...      | ...      | ...      | ...                             |
| ...    | ...    | ...    | ...    | 2194w    | ...      | ...      | ...                             |
| ...    | 2194w  | ...    | ...    | 2204vw   | ...      | ...      |                                 |
| 2783m  | 2790w  | 2786m  | 2808w  | ...      | ...      | ...      | $2\nu_{16}(F_2)$                |
| 2834vw | ...    | 2826vw | ...    | ...      | ...      | ...      | $\nu_6(E) + \nu_{16}(F_2)$ or   |
| 2868m  | 2864vw | 2864m  | ...    | ...      | ...      | ...      | $\nu_{15}(F_2) + \nu_{16}(F_2)$ |
| 2892vw | 2882sh | 2896vw | 2894w  | ...      | ...      | ...      |                                 |
| ...    | ...    | 2906vw | ...    | ...      | 2096sh   |          |                                 |
| ...    | ...    | 2112vw | 2110w  | 2111w    | 2104m    | 2108w    | $2\nu_6(E)$ or                  |
| 2914vw | ...    | 2132w  | 2126w  | 2124vw   | ...      | 2124vw   | $2\nu_{15}(F_2)$                |
| ...    | ...    | ...    | 2156sh | 2148sh   | ...      | ...      | ...                             |
| ...    | ...    | 2187m  | 2165s  | 2160s    | 2156s    | 2145s    | $\nu_1(A_1)$ + Lattice          |
| ...    | ...    | ...    | ...    | 2178vw   | ...      | 2164vw   |                                 |
| ...    | ...    | 2078vw | 2074vs | 2078vs   | 2073vs   | 2077vs   | $\nu_1(A_1)$                    |
| 2938vs | 2937s  | 2926s  | 2956s  | ...      | ...      | ...      |                                 |

Table 4.3 Contd....

| $d_0$    | $d_1$  | $d_3$  | $d_9$  | $d_{10}$ | $d_{11}$ | $d_{12}$ | Assignment                           |
|----------|--------|--------|--------|----------|----------|----------|--------------------------------------|
| ...      | ...    | ...    | 2227w  | ...      | ...      | ...      | ...                                  |
| ...      | ...    | ...    | ...    | ...      | 2984s    | ...      | $\nu$ (C-H)                          |
| ...      | 2223m  | ...    | ...    | 2220m    | ...      | ...      | $\nu$ (C-D)                          |
| ...      | 2970m  | ...    | ...    | 2968vs   | ...      | ...      | $\nu$ $\text{CH}_2\text{D}$<br>sym.  |
| ...      | ...    | ...    | ...    | 3010s    | ...      | ...      | $\nu$ $\text{CH}_2\text{D}$<br>asym. |
| ...      | ...    | ...    | ...    | ...      | 2174s    | ...      | $\nu$ $\text{CHD}_2$<br>sym.         |
| ...      | ...    | ...    | ...    | ...      | 2240vw   | ...      | $\nu$ $\text{CHD}_2$<br>asym.        |
| ...      | ...    | 2940w  | ...    | ...      | ...      | ...      | $\nu$ <sub>14</sub> ( $\text{F}_2$ ) |
| 2973w, b | ...    | 2952w  | ...    | ...      | ...      | ...      |                                      |
| 3010s    | ...    | 2266vs | 2266vs | 2250sh   | ...      | 2250w    | $\nu$ <sub>5</sub> (E) or            |
| 3015vs   | 3016vs | 3010vs | 3015vs | 2267vs   | 2266vs   | 2269vs   | $\nu$ <sub>13</sub> ( $\text{F}_2$ ) |
| ...      | ...    | ...    | 2300vw | 2298vw   | ...      | ...      | ...                                  |
| ...      | ...    | ...    | ...    | 2885w    | ...      | ...      | ...                                  |
| ...      | ...    | 2976vw | ...    | ...      | ...      | ...      | ...                                  |

v - very, s - strong, m - medium, w - weak, sh - shoulder and  
b - broad.

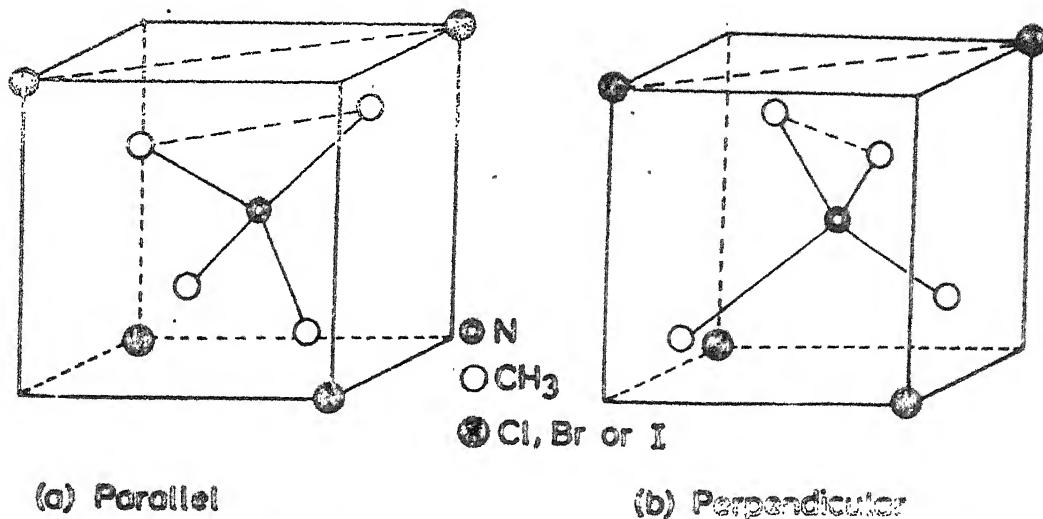


Fig. 4.1 Parallel and perpendicular orientations of the TMA ion in TMA halides (after Ohe [4]). Adjacent edges of the two tetrahedra (one formed by the methyl groups and the other by the four neighbour halide ions) are parallel (a), and perpendicular (b).

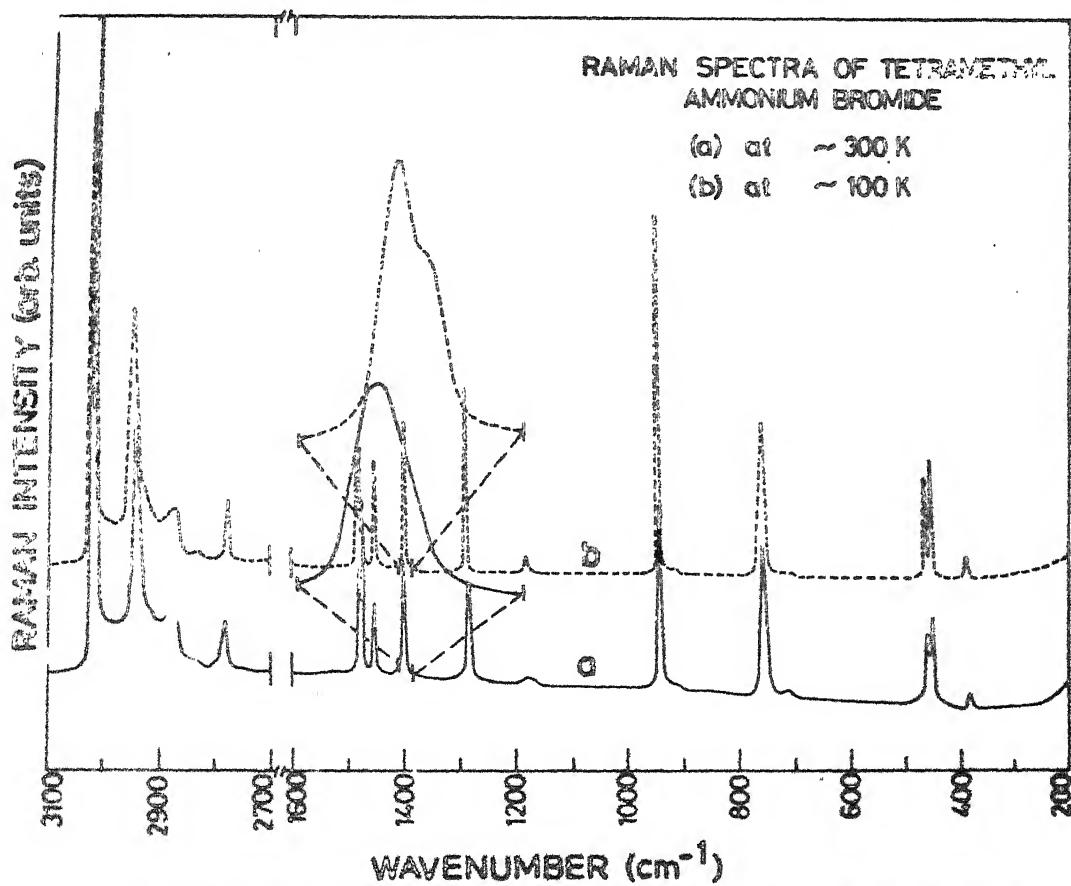


Fig. 4.2 Raman spectra of tetramethyl ammonium bromide (a) at 300 K and (b) at 100 K.

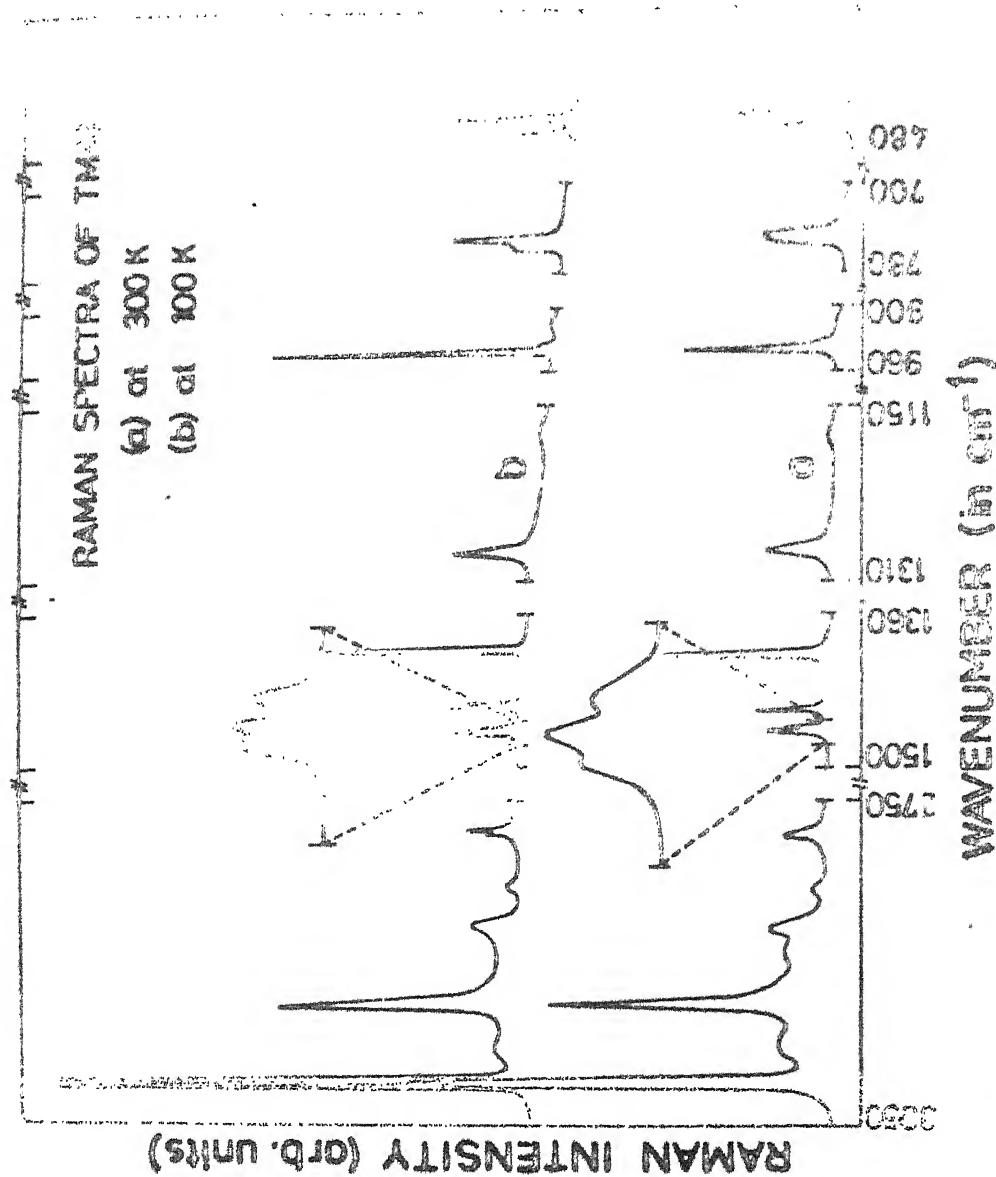


Fig. 4.3 Raman spectra of tetramethyl ammonium iodide (a) at 300 K and (b) at 100 K.

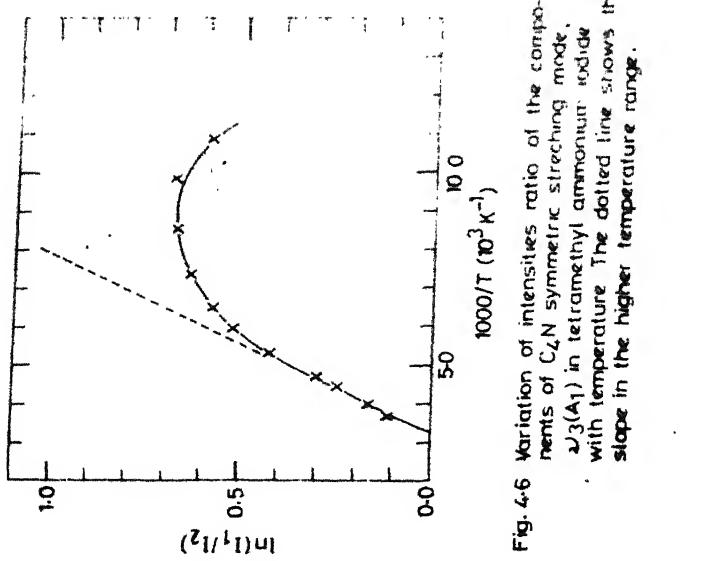


Fig. 4.6 Variation of intensities ratio of the components of  $C\equiv N$  symmetric stretching mode,  $\omega_{3(A_1)}$  in tetramethyl ammonium iodide, with temperature. The dotted line shows the slope in the higher temperature range.

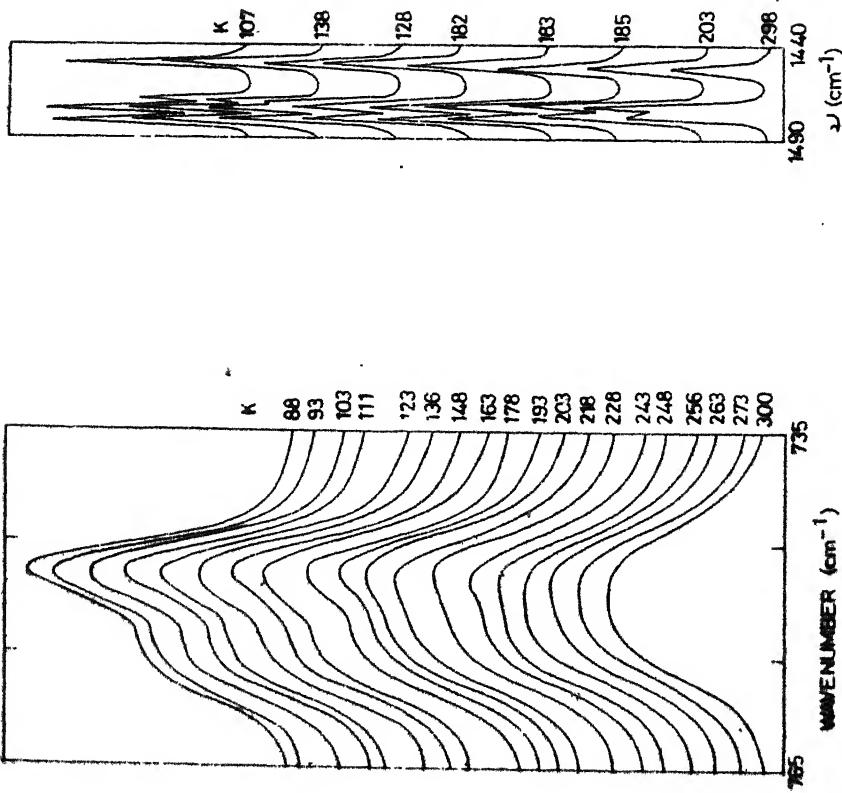


Fig. 4.5 The temperature dependence of  $CH_3$  asymmetric deformation  $\omega_{6(E)}$  and  $\omega_{15(F)}$  in tetramethyl ammonium bromide.

Fig. 4.4 Temperature dependence of the  $C\equiv N$  symmetric stretching mode  $\omega_{13(A_1)}$  in tetramethyl ammonium iodide

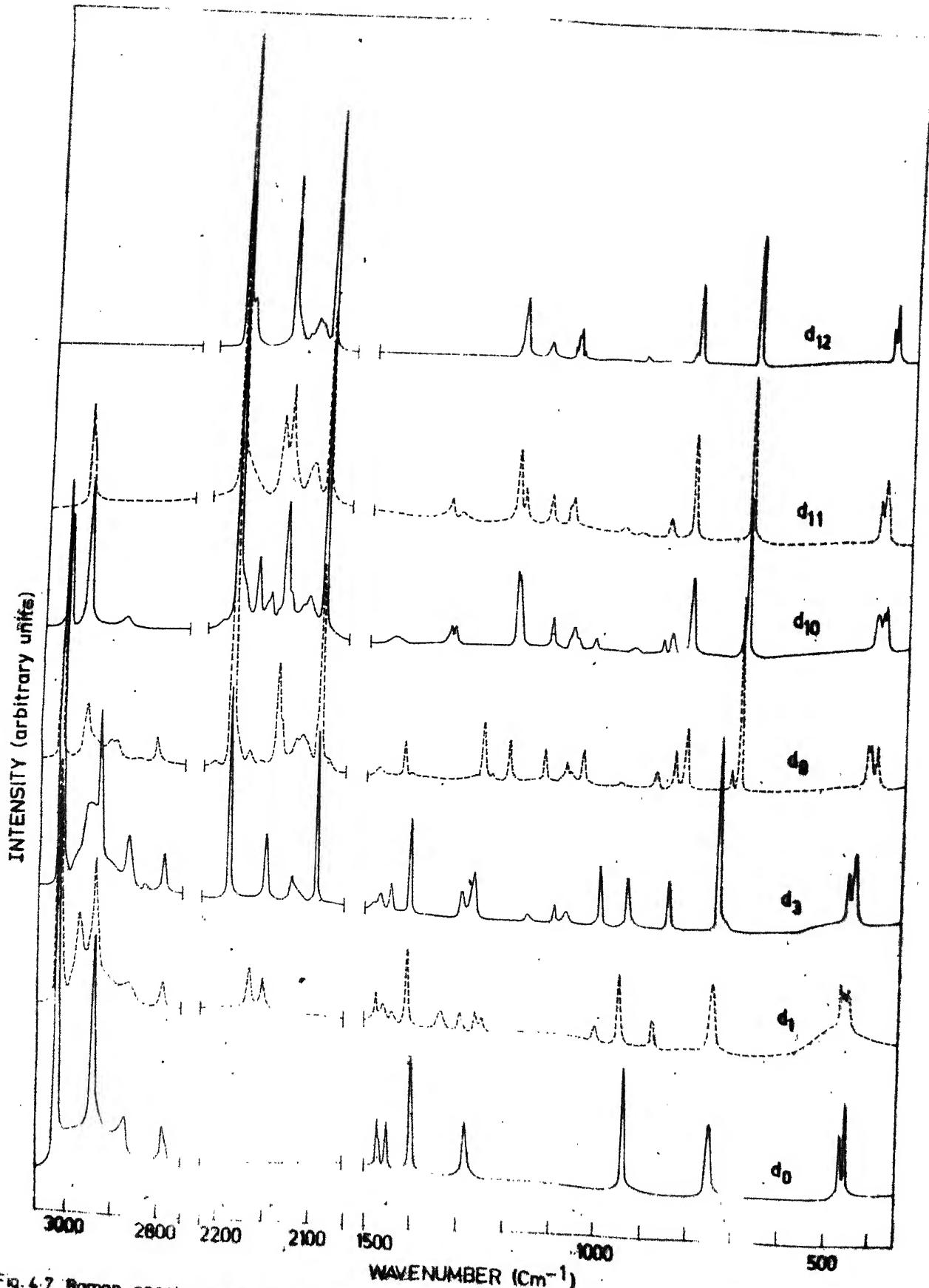


Fig. 4.7 Raman spectra of selectively deuterated tetramethyl ammonium iodide ( $\text{TMAI}-\text{d}_n$ ,  $n=0, 1, 3, 9, 10, 11$ , and 12) at room temperature.

## 5. INCOMMENSURATE PHASE IN TETRAMETHYL AMMONIUM TETRACHLORO ZINCATE

In this chapter we present our vibrational Raman studies on tetramethyl ammonium tetrachloro zincate (abbreviated as  $(\text{TMA})_2\text{ZnCl}_4$ ). We shall be mainly concerned with the behaviour of the internal modes in the incommensurate phase [1].

### 5.1 CRYSTAL STRUCTURE AND GROUP THEORETICAL ANALYSIS

The crystal structure of  $(\text{TMA})_2\text{ZnCl}_4$  at room temperature was first determined by Morosin and Lingafelter [2]. Wiesner et al. [3] reperformed the X-ray studies and modified the lattice parameters. It has an orthorhombic structure with space group  $P_{nma}$  ( $D_{2h}^{16}$ ) in which  $a = 12.276 \text{ \AA}$ ,  $b = 8.998 \text{ \AA}$ ,  $c = 15.541 \text{ \AA}$  and  $z = 4$ . The space group requires the  $\text{ZnCl}_4^{4-}$  and TMA tetrahedra to lie on mirror planes parallel to (010) and at  $y = \frac{1}{4}$ . All the atoms are in the position  $C_s(4)$  except Cl(2), Cl(3) and Cl(6) which are in the  $C_1(8)$  position.

For group theoretical analysis the TMA and  $\text{ZnCl}_4^{4-}$  have been considered as distinct groups which are at the site  $C_s$ . The total number of degrees of freedom for TMA in a unit cell are distributed as 24 translatory phonons + 24 rotatory phonons + 360 internal vibrations. For  $\text{ZnCl}_4^{4-}$  there are 12 translatory phonons + 12 rotatory phonons + 36 internal vibrations.

Table 5.1 illustrates the correlation between the species of point group  $T_d$  and factor group  $D_{2h}^{16}$  through the site symmetry  $C_S$ . The internal vibrations of TMA and  $ZnCl_4^{--}$  are distributed as follows:

$$\begin{aligned} \Gamma_{vib}^{TMA} = & 5A_g(R) + 4B_{1g}(R) + 5B_{2g}(R) + 4B_{3g}(R) \\ & + 4A_u + 5B_{1u}(IR) + 4B_{2u}(IR) + 5B_{3u}(IR) \quad (5.1) \end{aligned}$$

$$\begin{aligned} \Gamma_{vib}^{ZnCl_4^{--}} = & 6A_g(R) + 3B_{1g}(R) + 6B_{2g}(R) + 3B_{3g}(R) \\ & + 3A_u + 6B_{1u}(IR) + 3B_{2u}(IR) + 6B_{3u}(IR) \quad (5.2) \end{aligned}$$

The tensors associated with the Raman active species ( $A_g$ ,  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$ ) of the  $D_{2h}$  factor group in orthorhombic system are:

$$\begin{array}{c} A_{1g}: \left| \begin{array}{ccc} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{array} \right| \quad B_{1g}: \left| \begin{array}{ccc} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{yz} & 0 \end{array} \right| \\ B_{2g}: \left| \begin{array}{ccc} 0 & 0 & \alpha_{xz} \\ 0 & 0 & 0 \\ \alpha_{xz} & 0 & 0 \end{array} \right| \quad \text{and} \quad B_{3g}: \left| \begin{array}{ccc} 0 & \alpha_{xy} & 0 \\ \alpha_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{array} \right| \quad (5.3) \end{array}$$

An orthorhombic crystal could be examined under the following geometries:

|          |          |   |          |   |          |       |
|----------|----------|---|----------|---|----------|-------|
| $A_g$    | $z(xx)y$ | ; | $z(yy)x$ | ; | $y(zz)x$ |       |
| $B_{1g}$ | $z(yx)y$ | ; | $z(xy)x$ | ; | $y(xy)x$ |       |
| $B_{2g}$ | $z(xz)y$ | ; | $z(xz)x$ | ; | $y(xz)x$ |       |
| $B_{3g}$ | $z(yz)y$ | ; | $z(yz)x$ | ; | $y(zy)x$ | (5.4) |

Out of these twelve geometries, those belonging to  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$  species give only one distinct spectrum each. Thus a maximum of six different polarization spectra are expected in an orthorhombic system.

## 5.2 RAMAN SPECTRA OF $(TMA)_2ZnCl_4$ CRYSTAL

The relevant portions of the observed Raman spectra of  $(TMA)_2ZnCl_4$  at room temperature in six polarization geometries are shown in Fig. 5.1. The spectra are quite similar to those in aqueous solutions. Thus the vibrational (Raman) studies of  $(TMA)_2ZnCl_4$  support the results of Blinc et al. [4] from nuclear magnetic resonance measurements. Blinc et al. proposed that at room temperature the TMA ion has a number of equivalent orientational positions due to which  $(TMA)_2ZnCl_4$  behaves as a quasi-liquid. Our vibrational spectra reveal that  $ZnCl_4^{--}$  too has a number of equivalent orientational positions like TMA ion. The assignment of TMA modes in aqueous solution has been discussed in detail earlier [see Chap. 3]. The observed band-positions in  $(TMA)_2ZnCl_4$  and their assignment are given in Table 5.2.

The  $\nu_1^Z(A_1)$  and  $\nu_3^Z(F_2)$  modes of  $ZnCl_4^{--}$  under point group symmetry  $T_d$  are falling nearly at the same positions.

A sharp and strong band at  $280 \text{ cm}^{-1}$  in the diagonal polarizations which appears as a weak band in cross polarizations is assigned to  $\nu_1^Z(A_1)$ .  $\nu_3^Z(F_2)$  has negligible intensity in the Raman spectra and is covered by the overwhelming intensity of  $\nu_1^Z(A_1)$ . On the other hand,  $\nu_1^Z(A_1)$  is forbidden in IR spectra. A very strong band at  $272 \text{ cm}^{-1}$  appears in IR spectra and is assigned to  $\nu_3^Z(F_2)$ . The band at  $118$  and  $130 \text{ cm}^{-1}$  in  $X(ZZ)Y$  orientation are assigned  $\nu_2^Z(E)$  and  $\nu_4^Z(F_2)$ , respectively.

### 5.3 PHASE TRANSITIONS IN $(\text{TMA})_2\text{ZnCl}_4$

The sequence of successive phase transitions in  $(\text{TMA})_2\text{ZnCl}_4$  has been extensively studied by several techniques such as differential thermal analysis [5,6], X-ray scattering [7-10], neutron inelastic scattering [11], electron spin resonance [12,13], proton magnetic relaxation [4,14], dielectric measurement [15], ultrasonic wave propagation [16] etc. Six transitions are known to occur in the salt from room temperature down to liquid nitrogen temperature. The details about the phases and transition temperatures are compiled in Table 5.3.

The temperature dependence of the Raman spectra from a single crystal of  $(\text{TMA})_2\text{ZnCl}_4$  in the  $X(ZZ)Y$  orientation in the region  $2750-3100 \text{ cm}^{-1}$  is shown in Fig. 5.2. In this region we observed eight bands at  $3027$ ,  $2984$ ,  $2958$ ,  $2926$ ,  $2894$ ,  $2874$ ,  $2826$  and  $2810 \text{ cm}^{-1}$ . The band at  $3027 \text{ cm}^{-1}$  is associated with the  $\text{CH}_3$  asymmetric stretching modes and the

other bands are associated with the  $\text{CH}_3$  symmetric stretching mode and multiphonon transitions involving lower frequency bands.

The variation of the peak intensities with temperature of the four main bands at 3027, 2984, 2958, and 2926  $\text{cm}^{-1}$  in  $\text{X}(zz)\text{Y}$  orientation is shown in Fig. 5.3. At the  $\text{I} \rightarrow \text{II}$  transition point ( $T_i \approx 296 \text{ K}$ ) the intensities of the symmetric mode bands start decreasing and achieve a minimum value at 293 K. Below this temperature they again gain intensities till the next commensurate phase comes ( $T_c \approx 281 \text{ K}$ ). The  $\text{CH}_3$  asymmetric band at 3027  $\text{cm}^{-1}$  exhibits only marginal changes at the above transitions. The peak positions of all the bands remain unchanged. Such behaviour is observed for all the bands of species  $\text{A}_1$  under point group symmetry  $T_d$ . In the  $\text{X}(yz)\text{Y}$  geometry the behaviour is just the opposite, while in other geometries no temperature dependent variation of intensities is observed ( $\omega_{\text{I}}, \omega_{\text{II}}$ ) in this temperature range.

The existence of amplitudons and phasons is a specific feature of an incommensurate phase [17, 18]. The phasons can only be detected either by neutron inelastic scattering or by Brillouin scattering [17]. The soft mode behaviour of amplitudons in the lattice region and appearance of a band only in the incommensurate phase have been understood as the Raman signatures of an incommensurate phase [17, 18]. Bon et al. [19] have predicted the existence of a soft mode of species  $\text{A}_{1g}$  in the lattice region, but no such mode could be observed

in the lattice region in our spectra due to increase in the Rayleigh wing in going to low temperatures, which is perhaps related to the central peak problem.

As mentioned earlier Blinc et al. [4] have suggested that  $(TMA)_2ZnCl_4$  behaves as quasi-liquid, since it has a number of equally probable orientations. If one considers that in an incommensurate phase the orientations of  $(TMA)_2ZnCl_4$  are completely free relative to the X and Y directions, but with respect to the Z direction they have specific orientations which are governed by an incommensurate modulation in that direction, then a cosine term (cosine of angle between specific orientation and Z direction) will come in the expression for intensity of the bands and it may explain the abnormal behaviour of the intensity pattern. However, it could not so far be explained quantitatively. Efforts are in progress to understand theoretically the actual mechanism of such a behaviour of the internal modes in Raman scattering in the incommensurate phase.

#### 5.4 CONCLUSION

$(TMA)_2ZnCl_4$ , even in its crystalline state, behaves as a quasi-liquid on account of many equivalent orientational positions of both of its ionic entities, i.e., TMA and  $ZnCl_4^{2-}$ . It has many structurally distinct phases, out of which the incommensurate phase falling between the temperatures 290.6 and 280.5 K is of particular interest since all the totally

symmetric internal modes show an anomalous behaviour in this phase. A qualitative explanation for the observed anomaly is that the TMA and  $\text{ZnCl}_4^{2-}$  ions have discrete orientations about the Z-direction governed by an incommensurate modulation but are free to be at any angle relative to the X and Y directions.

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Table 5.1 : Correlation of molecular symmetry  $T_d$  to factor group  $D_{2h}$  through the site symmetry  $C_s$ .

| Molecular symmetry<br>$T_d$ | Site symmetry<br>$C_s$ | (xz) | Factor group<br>$D_{2h}$ |
|-----------------------------|------------------------|------|--------------------------|
| $A_1$                       |                        |      | $A_g$                    |
| $A_2$                       |                        |      | $B_{1g}$                 |
| $E$                         |                        |      | $B_{2g}$                 |
| $F_1$                       |                        |      | $B_{3g}$                 |
| $F_2$                       |                        |      | $A_u$                    |
|                             |                        |      | $B_{1u}$                 |
|                             |                        |      | $B_{2u}$                 |
|                             |                        |      | $B_{3u}$                 |

Table 5.2 : Observed band-positions (in  $\text{cm}^{-1}$ ) in the Raman spectra of  $(\text{TMA})_2\text{ZnCl}_4$  crystal at room temperature in six different polarization geometries and their assignment.

| $\text{Y}(XX)\text{Z}$ | $\text{X}(YY)\text{Z}$ | $\text{X}(ZZ)\text{Y}$ | $\text{X}(ZX)\text{Y}$ | $\text{X}(YX)\text{Y}$ | $\text{X}(YZ)\text{Y}$ | Assignment                               |
|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|--|
| 102vw                  | 96w                    | 102vw                  | ...                    | ...                    | ...                    | Lattice                                  |
| ...                    | 118w                   | 118w                   | 118w                   | 118w                   | 120w                   | $\nu_2^Z(\text{E})$                      |
| 138m                   | 132w                   | 130w                   | 130w                   | 130w                   | 138w                   | $\nu_4^Z(\text{F}_2)$                    |
| 280s                   | 284s                   | 284s                   | 276m                   | 280w                   | 280w                   | $\nu_1^Z(\text{A}_1)$                    |
| 372vw                  | 376vw                  | 372vw                  | 370vw                  | 376vw                  | 372vw                  | $\nu_8(\text{E})$                        |
| 460w                   | 458w                   | 464w                   | 458w                   | 458w                   | 460w                   | $\nu_{19}(\text{F}_2)$                   |
| 738w                   | 736w                   | 740w                   | ...                    | ...                    | 736vw                  | $2\nu_8(\text{E})$                       |
| 758vs                  | 760vs                  | 758vs                  | 756w                   | 756w                   | 756m                   | $\nu_3(\text{A}_1)$                      |
| 952m                   | 956m                   | 952m                   | 953w                   | 952w                   | 952w                   | $\nu_{18}(\text{F}_2)$                   |
| 1170vw                 | 1176vw                 | 1176vw                 | 1170vw                 | 1170vw                 | 1176vw                 | $\nu_7(\text{E})$                        |
| 1288vw                 | 1292vw                 | 1292vw                 | 1288vw                 | 1292vw                 | 1292vw                 | $\nu_{17}(\text{F}_2)$                   |
| 1416w                  | 1412w                  | 1412w                  | 1412w                  | 1412vw                 | 1416w                  | $\nu_{16}(\text{F}_2)$                   |
| 1452m                  | 1456m                  | 1454m                  | 1452w                  | 1456w                  | 1456w                  | $\nu_6(\text{E})$                        |
| 2808vw                 | 2810vw                 | 2810vw                 | ...                    | ...                    | 2808vw                 | $2\nu_{16}(\text{F}_2)$                  |
| 2826m                  | 2824m                  | 2826m                  | 2828vw                 | 2826vw                 | 2828w                  |  |
| 2876vw                 | 2874vw                 | 2874vw                 | ...                    | ...                    | ...                    | $\nu_{16}(\text{F}_2) + \nu_6(\text{E})$ |
| 2898vw                 | 2898vw                 | 2894vw                 | ...                    | ...                    | ...                    | $2\nu_6(\text{E})$                       |
| 2928s                  | 2926s                  | 2926s                  | 2928vw                 | 2928vw                 | 2928m                  | $\nu_6(\text{E}) + \nu_{15}(\text{F}_2)$ |
| 2960m                  | 2958m                  | 2958m                  | 2960vw                 | 2960vw                 | 2960w                  | $2\nu_{15}(\text{F}_2)$                  |
| 2984s                  | 2984s                  | 2984s                  | 2984vw                 | 2984vw                 | 2984w                  | $\nu_1(\text{A}_1)$                      |
| 3027s                  | 3028s                  | 3027s                  | 3028m                  | 3027m                  | 3026s                  | $\nu_5(\text{E}), \nu_{15}(\text{F}_2)$  |

Table 5.3 : The known phases and transition temperatures for  $(\text{TMA})_2\text{ZnCl}_4^*$ .

| Phase | Transition temperature | Space group  |
|-------|------------------------|--|
| I     | $296.65 \pm 0.05$ K    | $D_{2h}^{16}(\text{P}_{\text{nam}})$ $z = 4$ orthorhombic                        |
| II    | $280.95 \pm 0.05$      | Incommensurate $K_z = \frac{2}{5} +$   |
| III   | $277.40 \pm 0.06$      | $C_{2v}^9(\text{P}_{2_1\text{cn}})$ $z = 20$ orthorhombic<br>$K_z = \frac{2}{5}$ |
| IV    | $177.84 \pm 0.06$      | $C_{2h}^5(\text{P}_{2_1/c})$ $z = 12$ monoclinic                                 |
| V     | $170.65 \pm 0.06$      | $C_{2h}^5(\text{P}_{112_1/b})$ $z = 4$ monoclinic or<br>triclinic                |
| VI    | $159.01 \pm 0.06$      | ?  |
| VII   |                        | $D_2^4(\text{P}_{2_12_12_1})$ $z = 12$ orthorhombic                              |

\*From ref. [6].

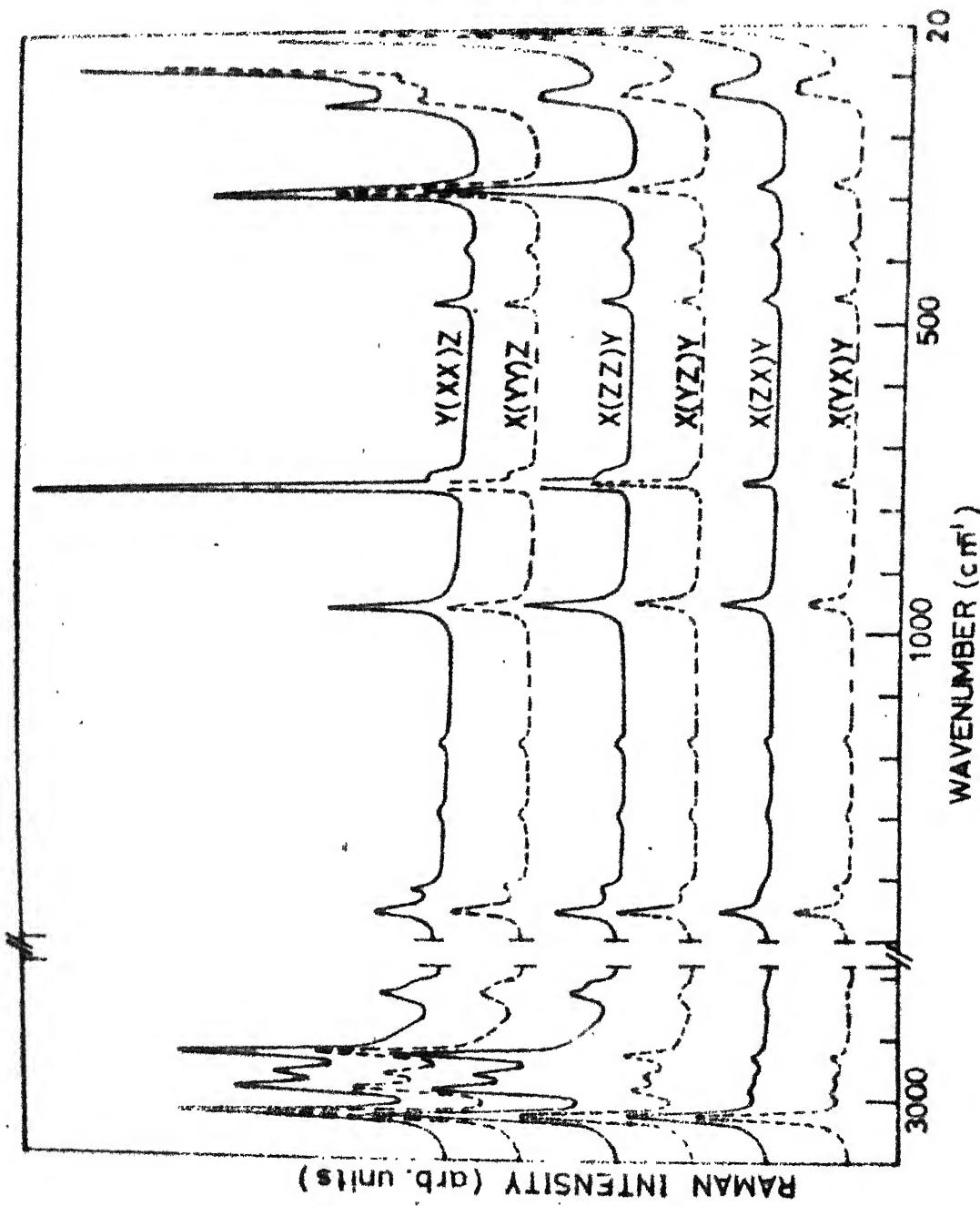


Fig. 5.1 Raman spectra of  $(\text{TMA})_2\text{ZnCl}_4$  at room temperature.

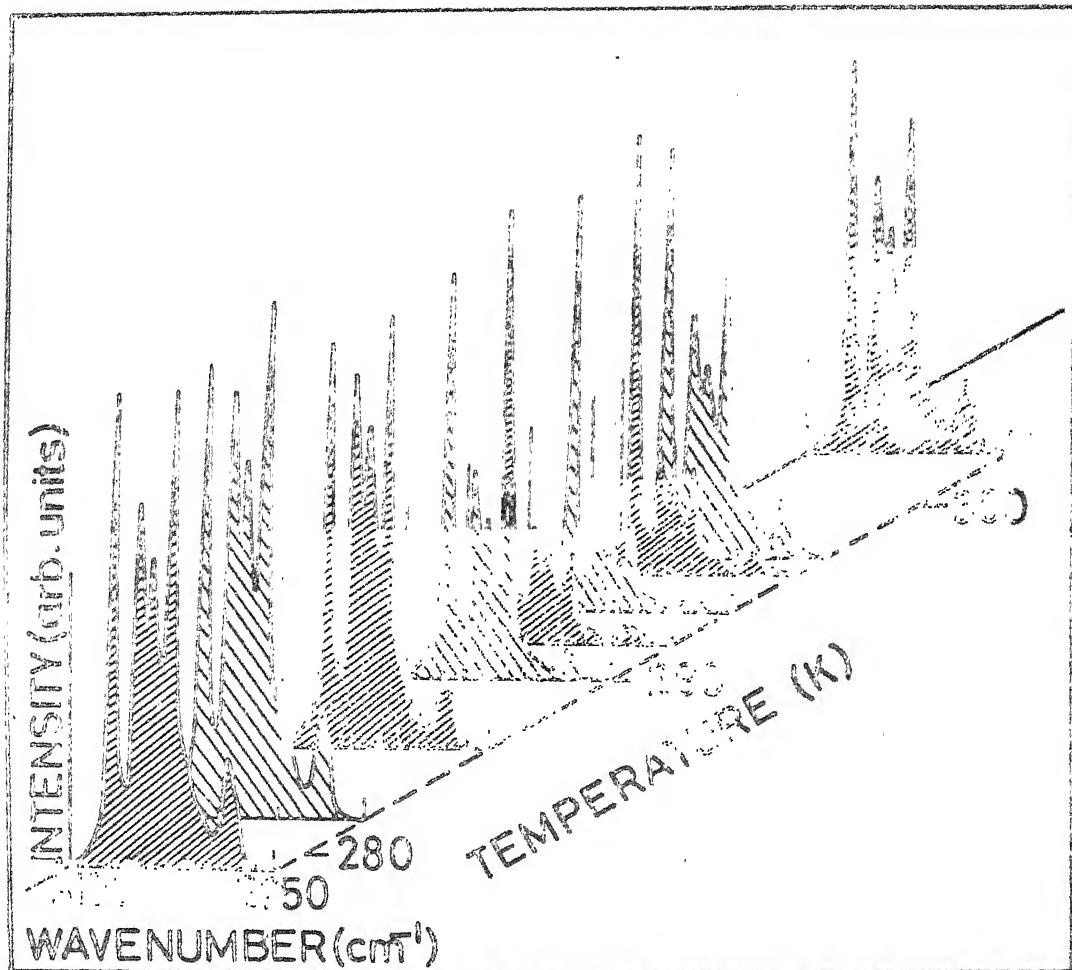


FIG.5.2 TEMPERATURE DEPENDENCE RAMAN SPECTRA OF  $[(\text{CH}_3)_4\text{N}]_2\text{ZnCl}_4$  CRYSTAL IN X(ZZ)Y POLARIZATION.

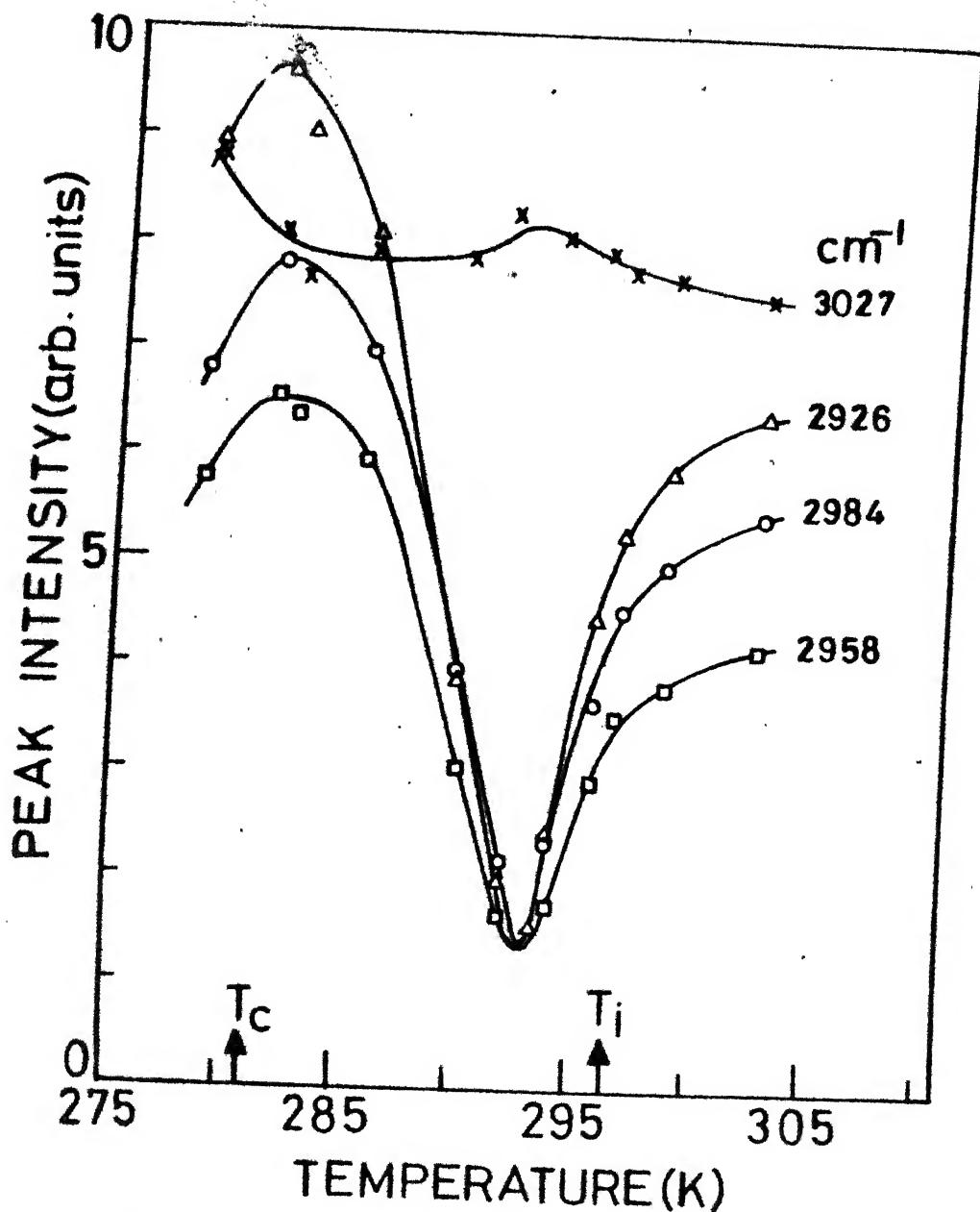


FIG.5.3 PEAK INTENSITY VERSUS  
TEMPERATURE OF THE BANDS  
IN X(ZZ)Y POLARIZATION.

## 6. CONCLUSION

In the work reported here the Raman and infrared absorption spectra of tetramethyl ammonium halides (chloride, bromide and iodide) and tetramethyl ammonium tetrachloro zincate have been studied with a view to understand the vibrational dynamics and the nature and mechanisms of the phase transitions in them. The observed bands in aqueous solutions and in solid phases have been characterized by considering the point group symmetry  $T_d$  of the tetramethyl ammonium (TMA) ion. The symmetric stretching mode of  $C_4N$  skeleton,  $\nu_3(A_1)$  shows a two-fold splitting in the iodide  $TMAI-d_O$ , unlike its single character in the corresponding chloride and bromide. This is attributed to reorientational disorder of TMA ion in the iodide between two inequivalent orientational positions - parallel and perpendicular; the reorientational energy has been calculated which turns out to be  $0.43 \text{ KCal mol}^{-1}$ . The tumbling would increase with the free space available in the lattice, and crystal data show it to be in the order  $TMAI > TMACl > TMABr$ . The maximum thermosensitivity of the bands is also found in TMAI for the same reason.

The asymmetric deformation modes of methyl group,  $\nu_6(E)$  and  $\nu_{15}(F_2)$ , which appear very close together at room temperature have been separately identified and assigned with

the help of the temperature variation studies of their Raman spectra. The Raman spectra of  $\text{TMA-d}_0$  halides in aqueous solutions show three intense polarized bands in the  $\text{CH}_3$  stretching region. Two models have been proposed to explain this : (i) anharmonicity and Fermi resonance, and (ii) dynamic distortion of  $\text{C}_4\text{N}$  skeleton. However, both the models fail to explain the appearance of only a single strong band in the  $\text{CH}_3$  symmetric stretching region in the Raman spectra of the polycrystalline  $\text{TMA-d}_0$  halides.

The three known phase transitions in  $\text{TMACl-d}_0$  above liquid nitrogen temperatures have been confirmed on the basis of these studies. Numbering the phases from high temperature downwards, the following inferences have been drawn about their mechanism from the spectral evidence : (i) the phase transition  $\text{II} \rightarrow \text{I}$ , occurring at 536 K, is due to ionic diffusion in which H atoms of  $\text{TMA-d}_0$  get relatively free, (ii) the transition  $\text{III} \rightarrow \text{II}$  is irreversible and of the reconstructive type and this transition temperature depends on the rate of heating,  $T_c$  going up as the heating rate is decreased. The transition occurs at  $367 \pm 2$  K on keeping the sample under vacuum during investigation, (iii) the transition  $\text{III} \rightarrow \text{IV}$  occurs at 185 K and is due to reorientation of  $\text{CH}_3$  groups and tumbling of the whole  $\text{TMAd}_0$  ion. In  $\text{TMACl-d}_{12}$  a single phase transition ( $\text{III} \rightarrow \text{II}$ ) at  $407 \pm 5$  K is observed which is irreversible and of the reconstructive type. It is concluded that  $\text{TMACl-d}_{12}$  lies in between  $\text{TMACl-d}_0$  and  $\text{TMABr-d}_0$  in the generalized phase diagram.

of the TMA halides. TMABr and TMAI do not undergo any phase transition in the temperature range 540 - 90 K.

Our studies have suggested that at room temperature  $\text{TMACl-d}_0$  and  $\text{TMABr-d}_0$  are isostructural, whereas  $\text{TMAI-d}_0$  possesses a different structure, though X-ray studies predicted the same space group for all the halides ( $D_{4h}^7$  ( $Z = 2$ )). Further X-ray diffraction studies and inelastic neutron scattering studies are needed to resolve this discrepancy. A space group for phase IV in  $\text{TMACl-d}_0$  is suggested to be  $D_4^1$  ( $Z = 2$ ) due to the splitting of bands of species  $F_2$  of  $\text{TMA-d}_0$  under molecular symmetry  $T_d$  into three components. In frame work of our studies the earlier suggested space group  $O_h^5$  ( $Z = 4$ ) for phase I is inherently inconsistent and has to be reinvestigated crystallographically.

$(\text{TMA})_2\text{ZnCl}_4$ , even in its crystalline state, behaves as a quasi-liquid on account of many equivalent orientational positions of both of its ionic entities, i.e., TMA and  $\text{ZnCl}_4^{--}$ . It has many structurally distinct phases and is incommensurate between the temperatures 290.6 and 280.9 K. In this phase, the totally symmetric modes behave anomalously in the z-direction due, probably, to discrete orientations of TMA and  $\text{ZnCl}_4^{--}$  ions about the z-direction governed by an incommensurate modulation.

Thus in terms of the experimental investigations and interpretation of data, this work is a substantial advancement for understanding molecular vibrational dynamics in tetramethyl ammonium halides and the nature and mechanisms of the observed phase transitions. The additional investigation of

tetramethyl ammonium tetrachloro zincate, a representative example of the series compounds which undergo successive phase transitions including an incommensurate phase, justifies the potentiality of the approach.

The systems, which have been the subject of the present work, provide many aspects for future studies. The most promising is the normal coordinate analysis for the calculation of the force constants and the vibrational frequencies. Efforts are under progress to work out a computer program for this purpose. These calculations will be very helpful in verification of the vibrational assignment. Besides this, in  $(TMA)_2ZnCl_4$ , the anomalous behaviour of the internal modes in the incommensurate phase seeks a theoretical justification. This, too, forms an interesting piece of work as the incommensurate phase transitions have, recently, attracted much attention for their peculiarity.

### LIST OF PUBLICATIONS

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